CERTIFICATE OF MAILING BY FIRST CLASS MAIL (37 CFR 1.8) Applicant(s): **Donald R. Huffman, et al.**			Docket No. **7913Z**	
Application No. **07/580,246**	Filing Date **9/10/1990**	Examiner **Stuart L. Hendrickson**	Customer No. **23389**	Group Art Unit **1754**

Invention: **NEW FORM OF CARBON**

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Appellants:	Donald R. Huffman, et al.	**Examiner:**	Stuart L. Hendrickson
Serial No.:	07/580,246	**Art Unit:**	1754
Filed:	September 10, 1990	**Docket:**	7913Z
For:	NEW FORM OF CARBON	**Dated:**	March 8, 2005
		Confirmation No.:	5441

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO NOTIFICATION OF NON-COMPLIANT APPEAL BRIEF UNDER 37 C.F.R. 41.37

Pursuant to the notification of non-compliant Appeal Brief under 37 C.F.R. §41.37, Appellants are filing herewith a new Appeal Brief which meets the requirements of 37 C.F.R. §41.37.

It is respectfully submitted that no official fees are required for filing this brief. However, if additional fees are required, the United States Patent and Trademark Office is authorized to charge those fees to Deposit Account No. 19-1013/SSMP. A duplicate copy of this paper is enclosed herewith.

Respectfully submitted,
Mark J. Cohen

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

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Dated: March 8, 2005

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BRIEF ON APPEAL

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APPELLANTS' BRIEF ON APPEAL

I. INTRODUCTION

Appellants, through their attorney, hereby submit this Brief on Appeal pursuant to 37 CFR §41.37 in response to the decision of the Examiner mailed October 7, 2003, finally rejecting claims 45-51, 53-75, 77, 80, 81, 83, 84, 86, 88, 89, 92, 93, 86-107 and 109-180.

II. REAL PARTY IN INTEREST

The real party in interest in the above-identified appeal who has been assigned the entire right, title and interest in the above-identified application is Fullerene International Corporation located at 9 East Loockerman Street, Dover Delaware

III. STATEMENT OF RELATED PROSECUTION

Copending Application having U.S. Serial No. 08/486,669 filed on June 7, 1995 is also on appeal. The '669 application is a continuation of U.S. Serial No. 236,933 filed on May 2, 1994, which is a continuation of U.S. Serial No. 855,959, filed on March 23, 1992, which is a

continuation of U.S. Serial No. 781,549 filed on October 22, 1991, which is a divisional of U.S. Serial No. 508,246, filed on September 10, 1990, which is a CIP of USSN 575,254 filed on August 30, 1990.

In addition, copending application having U.S. Serial No. 08/236,933 filed on May 2, 1994 is also on appeal. The '933 application is a continuation of U.S. Serial No. 07/855,959, filed on March 23, 1992, which is a continuation of U.S. Serial No. 07/781,549, filed on October 22, 1991, which is a divisional of U.S. Serial No. 07/508,246, filed September 10, 1990, which is a continuation-in-part of USSN 575,254 filed on August 30, 1990.

In addition, the present application, which was filed on September 10, 1990 was involved in Interference No. 103,201 in which priority was awarded to applicants Huffman and Kratschmer. A copy of the Decision is annexed in Appendix A to this Appeal Brief.

IV. STATEMENT OF SUPPORTING EDIVENCE

Evidence in support of this appeal is identified hereinbelow:

1. A Declaration of Raouf O. Loutfy, dated July 16, 2002, consisting of nine pages and two exhibits.
2. A Declaration of Harold W. Kroto under 37 CFR §1.132 dated July 27, 1995 consisting of six pages and seven exhibits ("Kroto I")
3. A Declaration of Harold W. Kroto under 37 CFR §1.132 dated June 9, 1995 having Serial No. 08/236,933, consisting of seven pages and six exhibits ("Kroto II')
4. A Supplemental Declaration of Harold W. Kroto under 37 CFR §1.132 dated November 16, 1999, having Serial No. 08/236,933 consisting of fourteen pages and six exhibits
5. An article entitled "Materials Science Abounds at the 1993 MRS Fall Meeting" in MRS Bulletin, page 54, March 1994

and Xerox copy of the Material Research Award

6. Certificate of the European Physical Society and accompanying article in Europhy. News 25, 1994.
7. Nobel Prize in Chemistry Award.
8. Article by Kratschmser, et al. in Nature, 1990.

These were all made of record at various times during the prosecution of the above-identified application. However, they were all listed and made of record with the Response dated July 17, 2002. Items 2, 5, 6, and 7 were also made of record in the interference. Copies are attached in Appendix B to the Appeal Brief.

V. STATEMENTS OF CLAIMS STATUS AND APPEALED CLAIMS

A. Statement of Claims

Claims 1-52 are cancelled.

Claims 53-72 are rejected under 35 USC §112, first paragraph, and 35 USC §§ 101 and 102/103.

Claim 73 is rejected under 35 USC §101 and 102/103.

Claim 74 is cancelled.

Claim 75 is rejected under 35 USC §101 and 102/103.

Claims 76-79 are cancelled.

Claims 80 and 81 are rejected under 35 USC §§101 and 102/103.

Claims 82 –83 are cancelled.

Claim 84 is rejected under 35 USC §102/103.

Claim 85 is allowed.

Claim 86 is rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 87-88 are cancelled.

Claim 89 is rejected under 35 USC §102/103.

Claim 90 is allowed.

Claim 91 is cancelled.

Claims 92-93 are rejected under 35 USC §101, and 102/103.

Claim 94 is allowed.

Claim 95 is allowed.

Claim 96 is rejected under 35 USC §112, first paragraph, 101, and 102/103.

Claims 97-101 are cancelled.

Claims 102-107 are rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 108-110 are cancelled.

Claims 111-114 are rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 115-118 are cancelled.

Claim 119 is rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 120-121 are cancelled.

Claims 122-132 are rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 133-140 are cancelled.

Claims 141-152 are rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claim 153 is rejected under 35 USC §101 and 102/103.

Claims 154 and 155 are rejected under 35 USC §112, first paragraph, 102/103 and 101.

Claim 156 is rejected under 35 USC §112, first and second paragraphs, 101 and 102/103.

Claim 157 is rejected under 35 USC § 112, first paragraph, 101 and 102/103.

Claims 158-161 are cancelled.

Claim 162 is rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 163-164 are cancelled.

Claims 165-170 are rejected under 35 USC §112, first paragraph, 101 and 102/103.

Claims 171-180 are cancelled.

B. Appealed Claims

Claims 53-73, 75, 80, 81, 86, 89, 90, 92, 93, 96, 102-107, 111-114, 119, 122, 123, 124-132, 141-157, 162, 165, 166, 167, 168, 169 and 170 are hereby appealed.

A clean copy of the claims pending is attached hereto in Exhibit C. Exhibit C1 recites the claims as they were on file as of July 17, 2002, prior to any Amendment filed after issuance of a Final Rejection, which subsequent Amendments were not entered, but excludes the claims that have been cancelled subsequent thereto. The cancelled claims are not being appealed. It is respectfully submitted that the cancellation of claims since July 17, 2002 does not imply in any way a concession by Appellants of the issues raised by the United States Patent and Trademark Office regarding those claims. Those claims have been cancelled without prejudice. Exhibits C2 lists the claims as amended in accordance with the Amendment filed contemporaneously herewith, which Applicants respectfully request be entered. It is those claims, as recited in Exhibit C2, which Appellants respectfully request be on appeal.

VI. STATEMENT OF AMENDMENT STATUS

An Amendment after Final Rejection dated May 19, 2004 was filed but was not entered. A second Amendment dated November 11, 2004, canceling claims 45-51, 74, 77, 83, 97-101, 109, 110, 115-118, 120, 121, 133-140, 158, 161, 163, 164 and 171-180, which simplified the issues on appeal, and made minor amendments to two additional claims, namely claims 72 and 156, was recently filed. In an Advisory Action mailed February 2, 2005, the United States Patent and Trademark Office has indicated that the claims have been broadened and that the Amendment will not be entered. Contemporaneously with this filing, an additional Amendment is being submitted. It is Appellants' intention to cancel the claims identified in the accompanying Amendment and to not broaden the scope of the remaining claims. Since this Amendment is being filed contemporaneously herewith, the United States Patent and Trademark

Office it has not acted thereon. Since it simplifies the issues, entry and consideration thereof is respectfully requested.

VII. SUMMARY OF CLAIMED SUBJECT MATTER ON APPEAL

The following is a summary of the subject matter defined in each of the independent claims:

Claim 53 is a product by process claim directed to make macroscopic amounts of C_{60}. More specifically, it is directed to a solid carbon product prepared by the process comprising:

(a) vaporizing a carbon source in the presence of an inert quenching gas under conditions effective to provide a sooty carbon product comprising C_{60} molecules;

(b) depositing the sooty carbon product on a collecting substrate;

(c) removing the sooty carbon product form the collecting substrate;

(d) contacting the sooty carbon product with a non-polar organic solvent effective to dissolve C_{60} molecules, said solvent being present in an amount effective to dissolve the C_{60} molecules in said sooty carbon product; and

(e) recovering from said resulting product formed when the sooty carbon product was contacted with said solvent a solid carbon product comprising C_{60} in a macroscopic amount.

Claim 73 is directed to a formed or molded product and comprising crystalline C_{60}.

Claim 75 is directed to free flowing particulate comprised of crystalline C_{60}.

Claim 80 is directed to a formed or molded product comprising solid C_{70}.

Claim 81 is directed to a free flowing particulate comprising solid C_{70}.

Claim 84 is directed to substantially pure C_{60}.

Claim 86 is directed to C_{60} in a macroscopic amount.

Claim 89 is directed to substantially pure C_{70}.

Claim 92 is directed to crystalline C_{60}.

Claim 93 is directed to crystalline C_{70}.

Claim 96 is directed to C_{70} in a macroscopic amount.

Claim 102 is directed to a macroscopic amount of substantially pure C_{60}.

Claim 103 is directed to a macroscopic amount of substantially pure C_{70}.

Claim 104 is directed to a formed or molded product comprising C_{70}, said C_{70} being present in a macroscopic amount.

Claim 105 is directed to a free flowing particulate comprising C_{70}, said C_{70} being present in a macroscopic amount.

Claim 106 is directed to a formed or molded product comprising C_{60}, said C_{60} being present in a macroscopic amount.

Claim 107 is directed to a flowing particulate comprising C_{60}, said C_{60} being present in a macroscopic amount.

Claim 111 is directed to a solid comprising C_{60}, said C_{60} being present in a macroscopic amount.

Claim 112 is directed to a solid comprising C_{70}, said C_{70} being present in a macroscopic amount.

Claim 113 is directed to a sooty product comprising C_{60}, the C_{60} in said sooty product being present in sufficient concentration to allow a macroscopic amount of said C_{60} to be separated therefrom.

Claim 114 is directed to a sooty product comprising C_{70}, the C_{70} in said sooty product being present in sufficient concentration to allow a macroscopic amount of said C_{70} to be separated therefrom.

Claim 119 is directed to a sooty carbon product prepared by the process comprising:

(a) vaporizing a carbon source in the presence of an inert gas to provide a vapor of carbon atoms,

(b) quenching said vapor of carbon in said inert gas under conditions effective to nucleate and condense said vapor of carbon atoms into a sooty carbon product comprising C_{60}

molecules, said C_{60} molecules being present in said sooty carbon in sufficient concentrations to allow a macroscopic amount of C_{60} to be separated from said soot.

Claim 141 is a directed to a solid carbon product prepared by the process comprising:

(a) evaporating a carbon source in the presence of an inert quenching gas under conditions effective to produce a sooty carbon product containing C_{60}, said C_{60} being present in said sooty carbon product in sufficient concentration to allow a macroscopic amount of said C_{60} to be separated from said sooty product;

(b) collecting the sooty carbon product produced therefrom;

(c) subliming the carbon product comprising C_{60} from the sooty carbon product; and

(d) condensing the sublimed carbon product comprising C_{60}.

Claim 165 is directed to a solid comprising a macroscopic amount of crystalline C_{60}.

Claim 166 is directed to a solid comprising a macroscopic amount of crystalline C_{70}.

Claim 167 is directed to a carbon product comprising a macroscopic amount of solid C_{60}.

Claim 168 is directed to a carbon product comprising a macroscopic amount of solid C_{70}.

Support for the subject matter in the independent claims is found in the specification. One of the issues on Appeal is whether there is support for the terms "macroscopic" and this is briefed hereinbelow, the contents of which are incorporated by reference. The support for the remaining subject matter is tabulated hereinbelow.

CLAIM #	SUPPORT
53	Page 3, lines 27-31
73	Original Claim 23, Page 14, lines 18-28
75	Original Claim 25
80	Original Claim 30, Page 14, lines 14-28
81	Original Claim 31, Page 14, lines 14-28
84	Original Claim 26
86	Page 3, line 26 to Page 5, line 28, Ex. 1-3
89	Original Claim 32
92	Page 14, lines 14-28
93	Page 14, lines 14-28
96	Page 7, Lines 20-25
102	Ex. 1
103	Page 13, line 13 to Page 14, line 29
104	Original Claim 30
105	Original Claim 31
106	Original Claim 23
107	Original Claim 25
111	Original Claim 14
112	Original Claim 28
113	Page 2, lines 18-24; Page 3, lines 28 to Page 5, line 16; Page 6, line 23 to Page 7, lines 10, Ex. 1
114	Page 2, lines 18-24, Page 3, line 28 to Page 5, line 16; Page 6, line 23 to Page 7, line 10, Ex. 1
119	Page 2, lines 18-24, Page 3, line 28 to Page 5, line 16; Page 6, line 23 to Page 7, line 10; Ex. 1
141	Page 2, lines 18-24, Page 2, line 28 to Page 5, line 16; Page 6, line 23 to Page 7, line 25
165	Original Claim 14, Page 8, line 6 to Page 11, line 26, Fig 1; Fig 2; Page 14, lines 14-28
166	Claim 28, Page 14, lines 14-28

VIII. GROUNDS FOR REVIEW

The first issue raised in the Office Action concerns Claim 53-72, 86, 96, 102-107, 111-114, 122-132, 141-153, 154-157, 162 and 165-170. The issue is whether there is adequate

written support in the specification, in accordance with 35 U.S.C. §112, first paragraph, for the term "macroscopic amounts" as used in the claims.

The second issue involves Claim 156 and the issue is whether Claim 156 complies with 35 U.S.C. §112, second paragraph and particularly points out and distinctly claims the subject matter which applicants regard as the invention.

The third issue is whether the subject matter in Claims 53-73, 75, 80, 81, 86, 92, 93, 96, 102-107, 111-114, 119, 122-132, 141-157, 162 and 165-170 is directed to a naturally occurring product.

The final issue is whether a reference, which alleges to have prepared C_{60} in quantities too small to see or feel and in quantities significantly less than in macroscopic amounts, anticipates or renders obvious claims directed to C_{60} and/or C_{70} in macroscopic amounts or the equivalent thereof.

It is to be noted that applicants have withdrawn from consideration and cancelled without prejudice Claims 45-52, 74, 76, 77, 83, 88, 97-101, 109, 110, 115, 116, 117, 118, 120, 121, 133-140, 158-161, 163-164 and 171-180. Thus, any rejection regarding any of these claims have been rendered moot. These claims should therefore not be considered at all in this appeal.

IX. ARGUMENTS

A. THERE IS ADEQUATE DESCRIPTIVE SUPPORT FOR THE TERM "MACROSCOPIC IN THE SPECIFICATION IN COMPLIANCE WITH THE DESCRIPTION REQUIREMENTS OF 35 U.S.C. §112, FIRST PARAGRAPH

1. The Subject Matter in Claims 53-72, 80, 107, 111-114 and 165-170 comply with the written description requirements of 35 USC §112, first paragraph

The term "macroscopic", as used in the rejected claims, is fully supported by the underlying specification. The term "macroscopic" as used in the rejected claims is used in association with amounts of C_{60} and/or C_{70}. Contrary to the allegations in the Final Rejection, in this context, there is adequate support, in accordance with the written description requirement of 35 U.S.C. §112, first paragraph, for the term "macroscopic amount" as it relates to C_{60} and/or C_{70}.

The written description requirement of 35 U.S.C. §112, first paragraph, provides that:

> [t]he specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise and exact terms so as to enable any person skilled in the art to which it pertains or with which it is most nearly connected to make and use the same... (emphasis added).

The written description requirement, which is distinct from the enablement and best mode requirements, serves to ensure that applicants have possession of the invention at the time of the filing of the application. In re Wertheim, 541 F.2d 257, 262, 191 USPQ 90, 96 (CCPA 1976). In order to meet the written description requirement, the applicant does not have to use

any particular form of disclosure to describe the subject matter, but the "description must clearly allow persons of ordinary skill in the art to recognize that [he or she] invented what is claimed." In re Gosteli, 872 F.2d 1008, 1012, 10 USPQ2d 1614, 1618 (Fed. Cir. 1989). In other words, the applicants must convey with reasonable clarity to the skilled artisan that as of the filing date he or she was in possession of the invention. Vas Cath., Inc. v. Mahurkar, 935 F.2d 1555, 1563-64, 19 USPQ 2d 1111, 1117 (Fed. Cir. 1991). Literal support is thus not necessary for compliance with the description requirement. Id.

There is adequate support in the application for the term "macroscopic" in the application. More specifically, support for this term and concept permeate the specification. For example, attention is directed to Example 1 of the instant specification wherein it is specified that the C_{60} product is obtained as a powder and wherein the color of the product produced therefrom is indicated. Obviously, the isolation of a product as a powder taken together with the fact that it is a colored powder connotes that the product could be seen with the naked eye, consistent with the use of macroscopic amounts recited in the claims. Furthermore, attention is directed to Page 7, Lines 10-25 of the specification, where it describes that when the sooty product was placed into a non-polar solvent, e.g., benzene, the benzene became colored and the product produced after extraction with the non-polar solvent is colored. Obviously, one cannot determine these characteristics unless the C_{60} was present in amounts that can be seen with the naked eye, i.e., macroscopic amounts. For example, if less than macroscopic amounts were produced, no color would be seen. (See, Curl, et al, Scientific American 1991, 54-55 who alleged to have isolated so little C_{60} that they were unable to obtain a colored solution thereof.) In addition, attention is directed to Page 11, Line 30 of the instant specification wherein it is indicated that the IR is

taken of an approximately two micrometer thick C_{60} coating on a silicon substrate. Especially since C_{60} is colored, it is obvious that this coating had to be seen with the naked eye. Furthermore, the application makes additional references to characteristics of the product that can only be discernible if the material is present in macroscopic amounts. For example, the application describes that the product produced by sublimation of the carbon soot can range from a uniform film to a coating, and the color is brown to gray depending on the thickness of the coat formed, while the product obtained from extraction is a dark brown to black crystalline material. Obviously, these characteristics, especially color, can be differentiated if the product was produced in amounts that can be seen with the human eye. In addition, on Page 2, Line 13, the application states that before the prior invention, no one had made C_{60} or C_{70} in "appreciable amounts." The implication is that the present inventors were successful in achieving this goal, consistent with the teachings in the application. Appreciable by definition means "enough to be perceived", See Webster Unbridged Dictionary 2nd Ed. p. 91 (1983). Thus, "appreciable" connotes large quantity, and is consistent with the term "macroscopic". All of these descriptions taken together as a whole connote that the C_{60} was produced in macroscopic amounts.

Moreover, by reading the section entitled "BACKGROUND OF THE INVENTION", the reader notes that throughout this section there is a comparison between the microscopic amounts of C_{60} described in the article by Kroto in Nature, vol. 1, 318, 162, 14 (1985) and the present invention. As stated in the instant application, "all that was observed [from Kroto to et al's work] was a peak in the mass spectra.... Kroto did not isolate any of said compound".

In contrast, as the section continues,...."No one has been successful in verifying the existence of this molecule since no one has been successful in isolating this molecule in

measurable amounts. Thus, no processes for producing recoverable amounts of this new compound have been described to the present time"(Emphasis added).

The application contrasts C_{70} of the Nature article with that of the present application in the following way:

"Another form of carbon containing 70 carbon atom (C_{70}) has also been postulated... Like the (C_{60}) to date, no one has been successful in verifying the existence of the C_{70}. Heretofore, no one has been successful in obtaining the molecule in any appreciable amounts."

The first sentence of the SUMMARY OF THE INVENTION says the following:

"A process has now been developed for the production of recoverable amounts of C_{60} and C_{70}".

When reading the passage, especially in context with the remainder of the specification, it becomes apparent to one of ordinary skill that the application describes a method and isolation of fullerenes, e.g., C_{60} and C_{70}, in amounts that were never realized heretofore. The understanding just from reading the beginning of the specification is that the application will describe how to make fullerenes, such as C_{60} and C_{70}, in amounts that would verify the existence of these molecules, C_{60} and C_{70}, for example in amounts sufficient to work with, in amounts sufficient to be seen with the naked eye, i.e., in macroscopic amounts.

This expectation is verified by one of ordinary skill in the art when reading the remainder of the specification.

For example, attention is directed to the Kroto Declaration dated June 9, 1995, ("Kroto I") especially Paragraphs 14 and 15, in which he attests that the application adequately describes

the method for making macroscopic amounts of fullerenes, such as C_{60} and C_{70}, and that based upon the teachings in the application, it is his opinion that the inventors had in their possession at the time of the filing of the application macroscopic amounts of same. Kroto, who is a skilled artisan in the field, and who won a Nobel Prize in Chemistry for discovering fullerenes, understood from reading the application that the applicants had made macroscopic amounts of e.g., C_{60} and had it in their possession at the time of the filing of the application, providing further evidence that there is adequate support in the specification for the term "macroscopic". A second Kroto Declaration ("Kroto II") further corroborates these statements. Yet, the Rejection never comments or discusses Dr. Kroto's testimony. Since a skilled artisan testified that the application describes the production of fullerenes, such as C_{60}, in macroscopic amounts, how can the United States Patent and Trademark Office ignore or dismiss such a statement? Case law has held that if a person of ordinary skill in the art would have understood from reading the specification that the inventor had possession of the claimed invention at the time of the filing of the application, then the written description requirement under 35 U.S.C. §112, first paragraph, is met. In re Alton, 76 F.3d 1168, 37 USPQ2d 1578 (Fed. Cir. 1996). The testimony from Dr. Kroto is undisputed factual evidence on this issue. In view of this evidence and in the absence of any evidence to the contrary, it is respectfully submitted that only one conclusion can be reached-- that the written description requirement under 35 U.S.C. §112, first paragraph is met.

Attention in this regard is also directed to the Supplemental Declaration of Harold W. Kroto under 37 C.F.R. §1.132 dated November 16, 1999. Dr. Kroto testifies that the specification provides evidence in several instances that the inventors had produced C_{60} and C_{70} in macroscopic amounts. For example, he refers to Example 1, which "describes the product

thereof in powder form as brownish-red. Such language connotes, in my opinion, that the product thereof could be seen with the naked eye..." This testimony supports the position of applicants.

Thus, Dr. Kroto's testimony clearly evidences that he read the application and that the application clearly conveys to one of ordinary skill in the art that the inventors had produced C_{60} and C_{70} in macroscopic amounts. This testimony cannot be ignored by the United States Patent and Trademark Office. See, In re Alton, 76 F.3d 1168, 37 USPQ2d 1578 (Fed. Cir. 1996).

Moreover, the application provides sufficient information for one of ordinary skill in the art to repeat the process described therein for making fullerenes, e.g., C_{60} and C_{70}. When this procedure is followed, macroscopic amounts of fullerenes, e.g., C_{60} and C_{70}, are produced. Thus, there is inherent support for the term "macroscopic amounts" of C_{60} and C_{70}.

Attention is directed to Paragraphs 15 and 17-19 of the Supplemental Delcaration of Harold Kroto, in which he testifies:

> 15. Moreover, based upon repetition of the process described therein, as described hereinbelow, the process as described in the above-identified application, especially in Example 1, inherently produces fullerenes, e.g., C_{60}, in amounts that could be seen with the naked eye.

Dr. Kroto further testifies in Paragraphs 17, 18 and 19 of the same Declaration as follows:

> 17. Utilizing the procedure exactly as described in the above-identified application, I have had fullerenes, including C_{60}, prepared in macroscopic amounts on numerous occasions since 1990 to the present. More specifically, by following the procedure described in the above-identified application and vaporizing graphite rods in an atmosphere of helium, forming the carbon soot therefrom, collecting the soot and dissolving

the soot in benzene, in accordance with the procedure described in the above-identified application, I and my colleagues have prepared and identified various fullerenes, including, inter alia, C_{60}...

18. Moreover, by following the procedure described in the above-identified application, and in accordance with the procedure outlined in Paragraph 17 herein, we have isolated fullerenes in macroscopic amounts, as defined herein. For example, utilizing the procedure outlined in Paragraph 17, I have found that the smoky carbon product contains 5 to 10% C_{60} and 1% C_{70}. We routinely produce the soot in 1-5 gram quantities and routinely extract 100-500 milligram amounts batchwise. Thus, one kilogram of sooty carbon product produces, on average, 100g of C_{60}, 10g of C_{70} and 1 gram of other fullerenes, such as those indicated hereinabove. The various fullerenes formed can and are isolated in accordance with the isolation and purification procedures described in the above-identified application, without an undue amount of experimentation. Furthermore, the various fullerenes are isolated as solids, which are easily visible to the naked eye. For example, in a typical experiment conducted according to the procedure described in the above-identified application, C_{60} is formed in about 100 mg quantities, C_{70} in about 10 mg quantities and the remainder in about 1 mg quantities.

19. Thus, by following the procedure described in the above-identified application, I have found that the process described therein inherently produces ... C_{60}, in macroscopic amounts. In fact, by following the procedure of Kratschmer and Huffman, outlined in the above identified application, crystalline material of fullerenes, including C_{60}, is produced which can be seen with the naked eye.

Thus, Dr. Kroto testifies that by following the procedure in the teachings in the above-identified application, one of ordinary skill in the art produces, inter alia, macroscopic amounts of C_{60} and/or C_{70}. In other words, Dr. Kroto testifies that C_{60} and/or C_{70} is inherently produced

in macroscopic amounts if one of ordinary skill in the art follows the teachings in the above-identified application for producing same.

Case law has held that words describing a function or property that was inherent in the specification is considered to be supported by the disclosure and supports the adequate written requirement, in accordance with 35 U.S.C. §112, first paragraph. See, In re Reynolds, 443 F.2d 384, 170 USPQ 94 (CCPA 1971). In Reynolds the question was whether words describing a function that was inherent in the claimed product could be added to the specification by amendment, or whether such description was "new matter". The Reynolds court cited with approval the holding in Technicon Instruments Corp. v. Coleman Instrument, Inc., 255 F.Supp. 630, 640-641, 150 USPQ 227, 236 (N.D. Ill. 1966), aff'd, 385 F.2d 391, 155 USPQ 369 (7th Cir. 1967), that: "By disclosing in a patent application a device that inherently performs a function, operates according to a theory, or has an advantage, a patent applicant necessarily discloses that function, theory, or advantage even though he says nothing concerning it." In re Reynolds, 433 F.2d at 389, 170 USPQ at 98. It was concluded that the express description of the inherent property, since not "new matter", could be added to the specification with effect as of the original filing date. Id.

Therefore, the disclosure in an application of an inherent property satisfies the written description requirement with respect to that property. Id., see also, Kennecott Corp. v. Kyocera International Inc., 835 F.2d 1419, 1422, 5 USPQ2d 1194, 1197 (Fed. Cir. 1987), cert. denied, 486 U.S. 1008 (1988).

This case not only is relevant but is instructive. Dr. Kroto's testimony indicates that the process described in the underlying application inherently produces C_{60} and/or C_{70} in

macroscopic amounts. In accordance with the holding of Reynolds, the inherent production of C_{60} and/or C_{70} in macroscopic amounts provides adequate support for the term "macroscopic" to be used in the claims.

Attention is further directed to the Declaration of Dr. Loutfy executed on July 16, 2002,containing 19 paragraphs (hereinafter "Loutfy Declaration"). Dr. Loutfy testifies that the process of the present invention inherently produces fullerenes, e.g., C_{60} and C_{70}, in macroscopic amounts (See Paragraph 11 of Loutfy Declaration). Dr. Loutfy further testifies that when he performed an experiment based upon the teachings in the underlying application, including Example 1, in which a graphite rod ¼ inch in diameter and 17 cm long, was vaporized at 100 torr Helium using 100 ampere dc current for about 50 minutes, he produced 12 grams of soot. He extracted the soot with toluene and the yield of fullerene was about 8 to 10%. Thus, he recovered over 1.2 grams of fullerene, with over 900 mg of C_{60} and over 200 mg of C_{70}. See paragraph 17 of Loutfy Declaration. Since amounts as low as 0.1 mg can be seen with the naked eye, this amount of C_{60} and C_{70} can be seen with the naked eye. Id.

Dr. Loutfy further testified that if he utilized a shorter length of graphite such as 1 cm length, as discussed in the underlying application including Example 1, he still produced macroscopic amounts of fullerene including 50 mg of C_{60} and 10 mg of C_{70}, which is still greater than the lower limit of 0.1 mg seen with the naked eye. Furthermore, if one calculates the amount of soot that would be produced from a 1 cm length and ¼ inch diameter graphite rod, the calculation would estimate that 633 mg of soot would be produced. Id. If one assumes 10% yield, then approximately about 66 mg of C_{60} and about 53 mg of C_{70} would be produced, which amounts are well above the amount that could be seen with the naked eye. Further, if a longer

graphite rod were used, the amount of C_{60} and C_{70} produced would be even greater. Again, this provides ample evidence that the C_{60} and C_{70} produced in accordance with the present process is in macroscopic amounts.

Attention is further directed to U.S. Patent No. 6,077,401, attached to the Loutfy Declaration which indicates in Column 2, lines 11-38 thereof that rods with ¼ inch diameter are capable of producing yields of around 15%. Consequently, since the amounts testified by Dr. Loutfy in the Loutfy Declaration assumed yields of 8-10%, this means that the amount of C_{60} and C_{70} produced in the experiment conducted by Dr. Loutfy can be even higher, further supporting appellants' position that the underlying application provides a process for producing C_{60} and C_{70} in macroscopic amounts.

Thus, there is no question that the process described in the underling application produces C_{60} and C_{70} in macroscopic amounts. The process described in the underlying application produces C_{60} and C_{70} in amounts that could be seen with the naked eye, which is the definition of macroscopic amounts used in the industry. See Paragraph 19 of Loutfy I Declaration. This usage is consistent with the way that Board of Patent Appeals and Interferences interpreted the term macroscopic as used in the instant specification. See Decision of the Board of Patent Appeals and Interferences dated September 23, 1999, Pages 30-37 (hereinafter, "Decision").

The Office Action dismisses the Loutfy Declaration alleging that it is speculative. Further, the Office Action further alleges that statements made by Loutfy in the Loutfy Declaration are conclusionary, stating that "it presupposes that macroscopic amounts of solid were deemed to have been prepared previously with different sizes of graphite."

Applicants strongly disagree. The statements by Dr. Loutfy are based on his experimental findings. Attention is directed to Paragraphs 17, et seq., of Loutfy Declaration which described the experiments performed by Dr. Loutfy upon which he bases his conclusions. As Dr. Loutfy testified, he repeated the process described in the above-identified application, and from his results, he calculated the amount of, inter alia, C_{60} and C_{70} produced by the process. From his data, Dr. Loutfy concludes that the C_{60} and C_{70} prepared by the process described in the instant application are each produced in amounts that are visible to the naked eye, that is, in macroscopic amounts. The point regarding changing the length of the rod was to emphasize the accuracy of the calculations made. Thus, the data provided in Dr. Loutfy's Declaration further supports that the inventors at the time of the filing of the instant application were in possession of macroscopic amounts of C_{60} and C_{70}.

Further, contrary to the allegations in the Office Action, color, in this instance, can be equated to macroscopic amounts. Attention is directed to the article by Curl and Smalley in Scientific American, 1991, referred to in the Office Action.

The author themselves equated color with macroscopic amounts. Attention is directed to Page 54, wherein the authors stated:

> "Thus for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet of the spectrum...
>
> In our laboratory we collected the sooty carbon produced by the vaporization base while using various chemical techniques to detect the presence of C_{60}. We slurried the soot in benzene, for example, and looked for a yellow color. But, the solution in our

> test tubes stayed clear, with boring black soot sitting on the bottom...
>
> When the Kratschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees and condense on a cold microscope slide to form smooth films of solid materials...
>
> In thin layers, these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying.)

Id. Pages 54-57.

As shown by the description in the article by the Nobel laureates, Smalley and Curl, color, i.e., "the yellow vial" was equated with "visible amounts" of product.

As one reads the article, it is quite apparent that the whole thrust of the article was to describe the procurement of visible amounts, i.e., macroscopic amounts, of C_{60} and C_{70}. They acknowledged that Huffmann and Kratschmer were they first to achieve this feat by repeating the process which is exemplified in the Nature article published in 1990 by Huffmann and Kratschmer attached in Exhibit B and which details are also described in the present application. Thus, they admit that Huffmann and Kratschmer were the first to isolate macroscopic amounts of same. They state, for example, that Huffmann and Kratschmer

> "... were the first to observe the roundest of all round molecules..."

Id. Page 54-57.

They "were looking at the first concentrated bottom of fullerenes ever seen."

Thus, they admit that the Huffmann-Kratschemr process produced macroscopic amounts of C_{60} and C_{70} by their process.

In fact the scientific community has recognized that the process of Huffman and Kratschmer, et al. which is exemplified in the article by Kratschmer, et al., Nature, 1990, 354, produces fullerenes, e.g., C_{60} or C_{70} in macroscopic amounts. Attention is directed to Column 1, lines 58-61 of U.S. Patent No. 6,077, 401, which is attached as Exhibit 2 to the Loutfy Declaration. The '401 patent indicates that Huffman and Kratschmer were the first to isolate macroscopic amounts of C_{60}. In addition, attention is directed to the article by Curl and Smalley in which they admit that Huffman and Kratschmer were the first to isolate fullerenes, e.g., C_{60} and C_{70}, in macroscopic amounts.

It is to be noted that Huffman and Kratschmer, along with Smalley and Kroto, were given the 1994 Hewlett Packerd Europphysics Prize by the European Physical Society for their discovery of fullerenes. In addition, only Huffman and Kratschmer and not Smalley, et al. were awarded the 1993 Materials Research Society Award for Synthesis and Pioneering Study of Fullerenes. These awards and the accompanying information show that Huffman and Kratschmer discovered fullerenes. Furthermore, the Swedish Academy in their press release awarding the Nobel Prize to Kroto, and Smalley, et al., acknowledged the contributions of Huffman and Kratschmer for being the first to make macroscopic amounts of fullerenes. The process which they used to isolate the C_{60}, C_{70} and other fullerenes in macroscopic amounts is the process which is described in the underlying application and exemplified in the Nature article. All of these items are in Exhibit B, appended to this Brief.

Accordingly, one can reach only one conclusion with respect to the issue of the written description for the term "macroscopic amounts of C_{60} and C_{70}"; that is, there is adequate support, in compliance with the description requirement of 35 U.S.C. §112, first paragraph for the term "macroscopic" amounts of C_{60} and C_{70}.

The facts of this case are similar to those In re Smythe, 480 F2d 1376, 198 USPQ 279 (CCPA 1973).

In Smythe, the invention related to a "continuous automatic analysis system where discrete liquid samples...are successfully introduced into an apparatus as a continuous stream, the individual samples being separated by a segmentizing medium." Both the specification and original claims identified this medium as "air or other gas which is inert to the liquid." The applicant later added claims that described the medium as "inert fluid". The United States Patent and Trademark Office rejected the added claims on the basis of the description requirement, but the Smythe Court reversed, stating that the use of the term "inert fluid" would naturally occur to the skilled art reading the description of the use of air or other gas as a segmenting medium to separate the liquid samples. Id. at 1377, 178 USPQ at 285. The court provided its rationale as follows:

> ....[W]hereas the broader concept of using "inert fluid" would naturally occur to one skilled in the art from reading appellants' description of the use and functions of the segmenting medium specifically described, we see no basis for denying appellants the claims which recite the segmenting medium broadly as "an inert fluid". The alternative places upon patent applicants, the Patent Office, and the public the undue burden of listing, in the case of applicants, reading and examining, in the case of the Patent Office, and printing and storing, in the case of the public, descriptions of the very many structural or functional equivalents of disclosed elements or steps which are already stored in the minds of those

skilled in the arts, ready for instant recall upon reading the descriptions of specific elements of steps.

> We are not saying that the disclosure of 'air or other gas which is inert to the liquid' sample by itself is a description of the use of all 'inert fluid' media. Rather, it is the description of the properties and functions of the 'air or other gas' segmentizing medium described in appellants' specification which would suggest to a person skilled in the art that appellants' invention includes the use of 'inert fluid' broadly...
> A hypothetical situation may make our point clear. If the original specification of a patent application on the scales of justice disclosed only a 1-pound 'lead weight' as a counterbalance to determine the weight of a pound of flesh, we do not believe the applicant should be prevented, by the so-called 'description requirement' of the first paragraph of '112, or the prohibition against new matter of '132, from later claiming the counterbalance as a 'metal weight' or simply as a 1-pound 'weight', although both 'metal weight' and 'weight' would indeed be progressively broader than 'lead weight', including even such an undisclosed, but obviously art-recognized equivalent, 'weight' as a pound of feathers. The broader claim language would be permitted because the description of the use and function of the lead weight as a scale counterbalance in the whole disclosure would immediately convey to any person skilled in the scale art the knowledge that the applicant invented a scale with a 1-pound counterbalance weight, regardless of its composition. (Emphasis in original)

The Smythe Court held that the description in the application "of air or other gas inert to the liquid" suggested to the skilled artisan the broader term. Similarly, as in Smythe, the present application supports the broader concept, "macroscopic amounts". It is the description of the color, the powder form collected, the measurements by x-ray, and the like, that connotes to one of ordinary skilled in the art the broad concept macroscopic. Furthermore, the testimony of Dr. Kroto corroborates that the application describes fullerenes to one of ordinary skill in the art at the time of the filing thereof.

Thus, contrary to the allegations in the Rejection, there is adequate support in the application for the term "macroscopic" amounts with respect to C_{60} and C_{70}. Thus, for the reasons provided herein, the rejection of Claims 53-72, 86, 107, 111-114, and 165-170 under 35 U.S.C. §112, first paragraph is in error, reversal thereof is respectfully requested.

2. <u>There Is Adequate Written Description In The Specification For The Sooty Carbon Product Recited In Claims 119, 122-132.</u>

As defined in the specification, the sooty carbon product is a product that comprises (contains) macroscopic amounts of C_{60} and C_{70}. The evidence and the rationale that support the conclusion that there is adequate support for the subject matter thereon is described hereinabove, the contents of which are incorporated by reference. Further evidence that the sooty carbon product contains macroscopic amounts of C_{60} and/or C_{70} is the fact that such amounts can be extracted to therefrom obtain a colored powdered or colored solution or colored film of C_{60} and/or C_{70}. The color of the products as well as the powder form can be discerned only if they were produced in amounts that could be seen with the naked eye, i.e., macroscopic amounts. Using the same rationale as described hereinabove, the contents of which are incorporated by reference, only are conclusion can be drawn -- macroscopic amounts were produced.

Therefore, the rejection of Claims 119, 122-132 under 35 U.S.C. §112, for allegedly lacking descriptive support is in error; reversal thereof is respectfully requested.

3. **There Is Adequate Written Description In The Specification For The Solid Carbon Product Described In Claims 141-162**

The description in the specification for the formation of the solid carbon product also complies with the description requirements of 35 U.S.C. §112, first paragraph. The application describes the isolation of the solid, and in fact exemplifies a solid comprising macroscopic amounts of C_{60}. Furthermore, a means of determining that the product was a solid comprised predominately of C_{60} was that it was sublimed and could be seen with the naked eye. It is to be noted that the application does not describe that the powder was only observed using instruments. The absence of such language connotes to one of ordinary skill in the art was that it was seen with the naked eye. Moreover, as shown by the data this powder was relatively pure and contained predominately C_{60}.

Moreover, it be to be noted that a element of the claim requires that macroscopic amount of C_{60} and/or C_{70} is separated from the sooty product by collecting and subliming the product and condensing the solid carbon product. Sublimation is a purification technique. What was collected was predominately C_{60}. Sufficient C_{60} had to be produced in order for the sublimed material to be removed off the collecting surface. In order to remove it off the collecting surface, it had to be seen. What was seen was crystalline C_{60}. See for example, Ex. 1. Thus, C60 was specifically exemplified to be made in macroscopic amounts.

Thus, the support and rationale for the subject matter in Claims 141-162 is the same as described above, the contents of which are incorporated by reference.

Therefore, for the reasons given herein, the rejection of Claims 141-162 for allegedly failing to comply with the written description requirement under 35 U.S.C. 112, first paragraph, is in error. Reversal of this rejection is respectfully requested.

B. AS AMENDED CLAIM 156 COMPLIES WITH THE REQUIREMENTS OF 35 U.S.C. §112, SECOND PARAGRAPH

The Final rejection lists 2 rejections under 35 U.S.C. 112, second paragraph for the following claims: 97-101, 109, 110, 115-118, 120, 121, 133-140, 156, 158-161, 171-180.

However, applicants have withdrawn and cancelled Claims 97-101, 109, 110, 115-118, 120, 121, 133-140, 158-161 and 171-180. The rejection of these claims is rendered moot. Thus, the only claim remaining is Claim 156.

Claim 156, as amended, recites that C_{70} can be separated from C_{60} by sublimation, column chromatography, fractional crystallization, capillary electrophoresis, preparative thin layer chromatography or extraction.

Appellants have removed the term "HPLC" from this claim in the latest amendment dated March 8, 2005. Since column chromatography is generic to HPLC, by this amendment, overlapping terms are removed.

Claim 156 as amended, describes separation techniques known to one of ordinary skill in the art. These are old techniques used for decades. Thus, the metes and bounds of the subject matter in Claim 156 is well understood by one of ordinary skill in the art. Therefore, the rejection of Claim 156 is overcome. Reversal thereof is respectfully requested.

C. CLAIMS 133, 134, 138 AND 161 HAVE BEEN CANCELLED, THE REJECTIONS THEREOF HAVE BEEN RENDERED MOOT.

Pursuant to the rejection of Claims 133-134, 138 and 161 under 35 U.S.C. §112, fourth paragraph, the Office Action alleges that these claims do not further limit the scope of the previous claim. However, inasmuch as applicants have canceled, without prejudice, Claims 133, 134, 138 and 141, the rejection of these claims is rendered moot.

D. THE REJECTION OF CLAIMS UNDER 35 U.S.C. §101 IS IMPROPER AS IT IGNORES LIMITATIONS RECITED IN THE CLAIMS

Pursuant to the rejection of Claims 45-51, 53-75, 77, 80, 81, 83, 86, 88, 92, 93, 96-107, and 109-180 under 35 U.S.C. §101, the Office Action alleges that these claims, absent the recitation of the term "macroscopic" or equivalent language thereto which the Office Action alleges is new matter - - a position with which applicants disagree- - embrace products found in nature. Applicants strongly disagree.

Before addressing the merits of the rejection, it is to be noted, as indicated hereinabove, that applicants have cancelled, without prejudice, Claims 45-51, 74, 77, 83,. 88, 97-101, 109, 110, 115-118, 120, 121, 133-140, 158-161, 163-164 and 171-180. Thus, the rejection of these claims under 35 U.S.C. §101 is moot; withdrawal thereof is respectfully requested.

Each of the claims pending recite the limitation of "macroscopic amounts of quantities" and/or equivalent language thereto. This language must be read into the claims and cannot be ignored. Moreover, as indicated by the Board of Patent Appeals and Interferences in its Decision, wherever C_{60} and/or C_{70} are found, they have not been found in macroscopic amounts. Attention is directed to the fact that the Board of Appeals and Interferences ruled in its Decision

dated September 25, 1999 that the scope of Claims 45-81, 83-86 and 88-180 are not unpatentable under 35 U.S.C. §101. See Page 49 of the Decision. The Office Action alleges, by referring to the earlier Action that this rejection only applies if applicants delete the term "in macroscopic amounts" in the claims. Inasmuch as this term or equivalent language thereto is recited in the pending claims, this rejection is not applicable. See, for example, Claims 53-72, 86, 96, 102, 103, 106, 107, 111-114, 119, 122-132, 141-157, and 162-170. Independent claims in which the term "macroscopic amounts" does not appear include Claim 73, which recites, "a formed or molded product comprising crystalline C_{60}"; Claim 75, which recites "a free flowing particulate comprised of crystalline C_{60}"; Claim 80, which recites "a formed or molded product comprising solid C_{70}"; and Claim 81, which recites "a free flowing particulate comprising solid C_{70}". But, no evidence has been presented that the products found in nature alleging to contain C_{60} or C_{70} is a formed or molded product, as recited in the claims. Thus, Claims 73, 75, 80, 81, and claims dependent thereon do not read on a natural product for still another reason.

The same rationale also applies to Claims 104-107. Although they recite that the C_{60} or C_{70}, is present in macroscopic amounts, they also recite, in addition, similar language. More specifically, Claims 104-107 are reproduced hereinbelow:

104. A formed or molded product comprising C_{70}, said C_{70} being present in a macroscopic amount.

105. A free flowing particulate comprising C_{70}, said C_{70} being present in a macroscopic amount.

106. A formed or molded product comprising C_{60}, said C_{60} being present in a macroscopic amount.

107. A free flowing particulate comprising C_{60}, said C_{60} being present in a macroscopic amount.

Again, since there is no evidence that in nature, wherever they are found, that C_{60} or C_{70} is present in a formed or molded product or a free flowing particulate. Thus, Claims 104-107 do not recite products of nature for a second reason.

Claims 92 and 93 are directed to crystalline C_{60} and C_{70}, respectively. However, no evidence has been presented that C_{60} or C_{70} when naturally found is crystalline. Thus, for still another reason, Claims 92 and 93 do not read on a natural product.

These are the only claims that are pending and are rejected which do not recite the term "macroscopic amounts therein". Thus, none of the rejected claims read on products of nature.

Moreover, Claims 113, 114, 119 and 123-32 do not read on products of nature for still another reason. None of the evidence provided by the United States Patent and Trademark Office refer to any sort of soot containing C_{60} or C_{70}, which is capable of deriving therefrom C_{60} or C_{70} in macroscopic amounts. This is quite apparent, especially since none of the articles cited by the United States Patent and Trademark Office found any soot containing any fullerenes - - let alone C_{60} or C_{70}. Furthermore, even assuming pro arguendo, that there was soot containing C_{60} or C_{70}, since C_{60} or C_{70} have not been found in macroscopic amounts in nature, any soot containing C_{60} and C_{70} would not be capable of producing C_{60} or C_{70} in macroscopic amounts. Thus, for the second reason, Claims 113, 114, 119 and 122-132 do not read on products of nature.

Finally, it is to be understood that the pending claims require that C_{60} and where applicable, C_{70}, be present in amounts that can be seen with the naked eye, i.e., in macroscopic amounts.

Thus, for the reasons presented herein, the rejection of Claims 45-51, 53-75, 77, 80, 81, 83, 86, 88, 92, 93, 96-107, and 109-180 under 35 U.S.C. §101 is in error, reversal of this rejection is respectfully requested.

E. THE CLAIMED SUBJECT MATTER IS NOT ANTICIPATED OR RENDERED OBVIOUS BY THE TEACHINGS OF KROTO, ET AL.

1. Summary

Kroto et al. never made macroscopic amounts of C_{60} or C_{70}, a requirement of the pending claims, a fact substantiated by Curl et al. At most tens of thousands of C_{60} were produced. This amount was too little to see with the naked eye or to even obtain a colored product. Thus, inasmuch as Kroto et al. never made C_{60} in macroscopic amounts, the teachings therein do not anticipate the subject matter in the claimed subject matter.

Moreover, inasmuch as Kroto et al. could not make C_{60} or C_{70} in macroscopic amounts, since the reference did not teach disclose or suggest C_{60} and C_{70} in macroscopic amounts and since it was not known prior to the filing of the application how to prepare C_{60} or C_{70} in macroscopic amounts, Kroto et al (with Curl et al. to show an inherent state of fact) do not render obvious the claimed subject matter.

2. Rejection Of Claims 45-51, 77, 83, 97-101, 109, 110, 115-118, 120, 121, 133-140, 158-161, 163, 164 And 177-180 Are Rendered Moot.

Inasmuch as applicants have cancelled without prejudice Claims 45-51, 77, 83, 97-101, 109, 110, 115-118, 120, 121, 133-140, 158-161, 163, 164 and 177-180, this rejection with respect to those claims is rendered moot.

3. Claims 86, 96, 102-107, 111-114, 119, 141, 162 And 165-168 Are Not Rejected Over Prior Art

The Final Office Action incorporates the prior art rejection from the Office Action of November 30, 1992 by reference. According to the incorporated Office Action, this rejection would apply to Claims 86, 96, 102-107, 111-114, 119, 141, 162 and 165-168 only if applicants delete the term "macroscopic amount" therefrom. However, applicants have not deleted the terms "macroscopic" therefrom. Thus, according to the Office Action, these claims are not rejected over the art.

4. It Is Improper To Reject Claims 122-132 And 142-162 Or 169-170 Over The Prior Art Since The Claims On Which These Claims Depend Are Not Rejected Over The Prior Art.

The United States Patent and Trademark Office has indicated that if the term "macroscopic" remains in the claims, the prior art rejections are not applicable. Since the term "macroscopic" was not deleted from Claim 119, 141 and 167-168, the United States Patent and Trademark Office has indicated that the subject matter therein is not rejected under 35 U.S.C. §102/103 over Kroto et al. In other words, the United States Patent and Trademark Office has indicated that these claims, as written, are novel and non-obvious over the cited prior art.

However, the United States Patent and Trademark Office has rejected Claims 122-132, 147-157, 162, 169 and 170, which are ultimately dependent upon these independent claims over the same prior art. This rejection is not logical. Moreover, these rejections are inconsistent with case law. Dependent claims are patentable over the prior art if the independent claims from which they depend are patentable over the prior art. See, e.g., In re Fine, 837 F2d 1071, 1076, 5

USPQ2d 1596, 1680 (Fed Cir 1988) ("Dependent claims are non-obvious under Section 103 if the independent claims from which they depend are non-obvious.)

Accordingly, since Claims 122-132 are dependent upon Claim 119, and since, according to the Office Action, Claim 119, is not rejected over the prior art, it follows that the subject matter of Claims 122-132 cannot be rejected over the prior art.

Moreover, using the same rationale, since Claims 142-157 and 162 are dependent upon Claim 141 and since Claim 141 is not rejected over the prior art, then it also follows that the subject matter of Claims 142-157 and 162 cannot be rejected over the prior art.

Finally since Claims 169 and 170 are dependent upon Claims 167 and 168 respectively, and since the latter claims are not rejected over the prior art, it also follows that Claims 169 and 170 cannot be rejected over the prior art.

Thus, the rejection of all of these claims is improper. Reversal thereof is respectfully requested.

5. The Prior Art Does Not Teach, Disclose Or Suggest Any Solid Containing Macroscopic Amounts Of C_{60} Or C_{70}.

The remaining rejected claims recite crystalline C_{60} or C_{70} or solid C_{60} or C_{70} or solid C_{60} containing macroscopic amounts of C_{60}. (See, e.g., Claims 53 and claims dependent thereon, 73, 75, 80, 81, 92, 93) or substantially pure C_{60} or C_{70} (See, e.g., Claims 84 and 89). Each of these claims are argued separately. Thus, for example, Claims 84 and 89 are argued separately from the other claims.

Kroto, et al. never isolated any solid or comprising crystalline C_{60} or C_{70}, or C_{60} in solid from containing macroscopic amounts. In fact, they never isolated any product in the solid form at all. Thus, the pending claims are patentable over the prior art.

Kroto, et al. report on the detection of C_{60} and C_{70} using time of flight mass spectrometry in the vapor phase. However, they never isolated or recovered visible particles of C_{60} and C_{70}. They never produced C_{60} or C_{70} as a solid or in solid form, let alone crystalline C_{60} or C_{70}. See, Curl, et al. See, also Loutfy Declaration Paragraph 12. In addition, they did not disclose a process that would teach or lead others to do so. See, Curl, et al. and Loutfy Declaration, Paragraph 2. Kroto, et al. admit that they only C_{60} made in small amounts. As described in Curl, et al., on page 54,

> they could "not collect more than a few tens of thousands of the special new molecules [fullerene]. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect... For now, the fullerenes existed only as fleeting signals."

No matter how much they tried they were always unsuccessful in making amounts sufficient to see, i.e., macroscopic amounts.

Thus, Curl, et al., on commenting about the experiments described in Kroto, et al. admit that they could not make enough to collect the fullerenes as a solid or in solid form or in macroscopic amounts or equivalent language thereto. Thus, contrary to the allegations in the Office Action, Kroto, et al. never made a solid comprising solid or crystalline C_{60} or C_{70}, since Kroto, et al. never made enough to collect a crystalline or solid C_{60} or C_{70}. Thus, the process of Kroto, et al. was not capable of making sufficient amounts of C_{60} or C_{70} to make crystalline C_{60}

or C_{70}. The process of Kroto, et al. never formed C_{60} or C_{70} or other fullerenes in any amounts that could be seen with the naked eye or isolated as such as a solid, whether it be in the soot or not. They never prepared solid C_{60} or solid C_{70}. Kroto never made C_{60} or C_{70} in amounts that could be seen, touched or felt. They never made C_{60} or C_{70} in macroscopic amounts. Since they made only a few molecules of fullerenes, they could never isolate C_{60} or C_{70} in solid form, as claimed. Moreover, as a consequence thereof the soot formed in the Kroto, et al. process is not comprised of solid particles consisting essentially of C_{60} or C_{70} or soot capable of producing C_{60} or C_{70} in macroscopic amounts, as claimed.

Thus, the claimed subject matter differs from the subject matter described in Kroto in at least one aspect. The claims, as defined, recite greater amounts than that described in Kroto, et al. Since anticipation under 35 U.S.C. §102 requires that the prior art reference discloses each and every element of the claims, and since the absence of an element in the claim relative to the prior art negates anticipation, inasmuch as Kroto, et al. do not disclose the C_{60} and C_{70} being present in the amounts claimed - - an important element of the claims- - the claimed subject matter in the rejected claims does not anticipate the present invention.

Moreover, applicants respectfully submit that the Kroto, et al. article is non-enabling to make fullerenes, e.g., C_{60} or C_{70} in macroscopic amounts or language equivalent thereto, e.g., solid form, as a solid, in macroscopic amounts or in equivalent language.

They never prepared solid or crystalline C_{60} or C_{70}, as presently claimed. It was not possible to prepare C_{60} or C_{70} solid or, for that matter, C_{60} or C_{70}, in any appreciable amounts, without undue experimentation. As stated in Curl, et al., despite extensive efforts by the scientific community, no one prior to Kratschmer and Huffmann was successful in preparing C_{60}

or C_{70} in any appreciable amounts. Consequently, Kroto, et al. do not teach, disclose, or even suggest solid C_{60}, or solid C_{70}, crystalline C_{60}, crystalline C_{70}, solids consisting essentially of C_{60} or C_{70}, etc., or any matter comprised of solid C_{60} or C_{70} as presently claimed.

To be enabling, a reference must describe an invention sufficiently to have placed the public in possession of it. In re Donahue, 766 F.2d 531, 226, USPQ 619 (Fed. Cir. 1985). The printed publication must be enabling. Constant v. Advanced Micro-Devices, Inc., 848 F.2d 1560, 7 USPQ 21 1057 (Fed. Cir. 1988). The test of enablement is whether one reasonably skilled in the art could make or use the invention from the disclosure in the reference coupled with the information known to one skilled in the art without undue experimentation. United States v. Teletronics, Inc., 857 F.2d 778, 775 8 USPQ 21 1217 (Fed. Cir. 1988), cert. denied 109 S.Ct. 1954 (1989).

But, the public was not possessed of a method of preparing, isolating, and C_{60} and C_{70}, in the amounts claimed in the present application, including a C_{60} or C_{70} in the solid state. Based on the teachings by Kroto, et al., people skilled in the art were unsuccessful in preparing macroscopic quantities of C_{60} or C_{70}. Despite extensive efforts, no solid of C_{60} or C_{70} could be made or isolated until these were prepared and isolated by the present inventors. Furthermore, despite extensive efforts, no crystalline C_{60} or C_{70} was ever prepared and isolated by others prior to the filing date of the instant application. Further, no material containing solids comprising solid C_{60} and/or solid C_{70} were made until the present inventors developed the methodology. Thus, Kroto, et al. did not place the public in possession of the applicants' invention.

> It is well settled that prior art under 35 U.S.C. §102(b) most sufficiently describe the clamed invention to have placed the public in

> possession of it .... Such possession is effected if one of ordinary skill in the art could have combined the publication's description of the invention with his own knowledge to make the claimed invention. Accordingly, even if the claimed invention is disclosed in a printed publication, the disclosure will not suffice as prior art if it was not enabling... In re Donahue, 766 F.2d 531, 533, 226 USPQ 619, 621 (Fed. Cir. 1985).

Moreover, the Court continues that if the reference teaches that attempts to make the invention failed, as in the present case, the reference is non-enabling:

> ...In those cases, the references were deemed insufficient because they stated that attempts to prepare the claimed compounds were unsuccessful. Such failures by those skilled in the art (having possession of the information disclosed by the publication) are strong evidence that he disclosure of the publication was non-enabling. Id.

Furthermore, Kroto, et al. were completely unsuccessful in making, isolating and collecting C_{60} and C_{70} in any appreciable amounts. They only had indirect evidence of what it is that they made. They never made solid C_{60} and C_{70}. They never made or isolated a crystalline form of C_{60} and C_{70}. Whatever they made, they only made it in non-measurable amounts. At best, they could only make molecules of something, only tens of thousands of molecules, which they could not touch, see or smell. No matter how much they tried, they were always unsuccessful in making more. They could never make enough material to put it in the possession of the public:

> Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the vial" because quantum calculations for such a soccer ball shaped carbon molecule suggested it would absorb light strongly only in the far violet of the spectrum....

Curl, et al. at 55.

Contrary to the allegations the Office Action, Kroto, et al. did not make the amounts of fullerenes, e.g., C_{60} or C_{70} in the amounts recited in the rejected claims or place the public in possession thereof. Thus, Kroto, et al. is non-enabling for making the amounts claimed in the present process and cannot be used for that purpose.

Moreover, the rationale of why Kroto, et al. never made macroscopic amounts of C_{60} or C_{70} is described in Dr. Loutfy's Declaration. Dr. Loutfy distinguishes the process of the present invention from that of Kroto, et al. See paragraph 15 of the Loutfy Declaration. More specifically, unlike the prior art, including the process of Kroto, et al., the present process produces a high density of carbon vapor, as described on Page 4 of the subject application, resulting in the formation of macroscopic amounts of fullerenes by the present method. Id. The Kroto, et al. process could not produce a high density of a vapor of carbon. Since Kroto, et al. could not produce a high density of a vapor of carbon by their process, they could not provide C_{60} or C_{70} in macroscopic amounts or as a solid or crystalline solid. Thus, Claims 53 et seq. and the other claims reciting macroscopic amounts therein are patentable over the teachings of Kroto, et al.

Further, since Kroto, et al. never isolated any fullerenes, including C_{60} and C_{70} in any appreciable amounts, the soot containing same never was capable of producing C_{60} or C_{70} in macroscopic amounts, as recited in Claims 113, 114 and 119-132.

Moreover, there is no evidence that Kroto, et al. produced substantially pure C_{60} or substantially pure C_{70}, as recited in Claims 84 and 89. Kroto, et al. never isolated substantially

pure C_{60} or C_{70} per se. In the experiments, described in Kroto, et al. Kroto, et al. vaporized graphite using laser in a helium atmosphere. The species found may have been ionized at this point. But, even if not ionized, any C_{60} or C_{70} species formed was part of a gaseous mixture, in which the majority of the material was soot (amorphous carbon). As part of a mixture, any neutral C_{60} or C_{70} formed was not substantially pure. The mixture was then (further) ionized and separated in a time-of-flight mass spectrometry. In the mass spectrometer, positively charged fragments were formed. The mass spectrometer then separated the positively charged species. Thus, Kroto, et al. never formed substantially pure C_{60} or C_{70}, since any C_{60} or C_{70} initially formed was a small percentage of a gaseous mixture; and when separated, each was positively charged. Thus, the subject matter in Claims 84 and 89 is not anticipated by Kroto, et al.

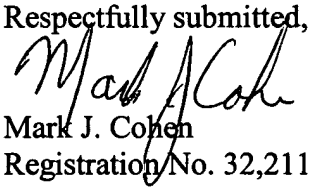
Further, Kroto, et al. never taught, disclosed or suggested C_{60} or C_{70} in macroscopic amounts or in amounts sufficient to isolate as a solid, and the like. The teachings therein are limited to the miniscule amounts described. Further, Kroto, et al. never taught how to make macroscopic amounts of C_{60} or C_{70} or in any amount sufficient to isolate as a solid, and the like. Thus, since one of ordinary skill in the art could not make these amounts of C_{60} or C_{70}, based on the teachings of Kroto, et al. Kroto, et al. do not teach disclose or suggest C_{60} or C_{70} in those amounts. Finally, since Kroto, et al. never made substantially pure C_{60} or C_{70}, Kroto, et al. never disclosed, described or suggested substantially pure C_{60} or C_{70}, as recited in Claims 84 and 89, respectively.

Thus, the rejection of the specified claims over the prior art is in error. Reversal thereof is respectfully requested.

X. CONCLUSION

The above arguments clearly overcome the rejections in the Final Action and clearly establish that all of the claims on appeal are patentable. Affirmance of the patentability and reversal of the Final Rejection of the claims on appeal is respectfully requested.

Respectfully submitted,



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THIS OPINION WAS NOT WRITTEN FOR PUBLICATION

The opinion in support of the decision being entered today (1) was not written for publication in a law journal and (2) is not binding precedent of the Board.

Paper No. 84

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

MAILED

SEP 23 1999

PAT.&T.M. OFFICE
BOARD OF PATENT APPEALS
AND INTERFERENCES

RONALD F. ZIOLO
Junior Party[1]
v.
JOSEPH MORT and MARY A. MACHONKIN
Junior Party[2]
v.
RONALD F. ZIOLO
Junior Party[3]
v.
DONALD R. HUFFMAN and WOLFGANG KRÄTSCHMER
Senior Party[4]

Interference No. 103,281

[1] Patent Number 5,232,810, granted August 3, 1993, based on Application 07/961,984, filed October 16, 1992. Assignor to Xerox Corporation, Stamford, Connecticut. (Ziolo I).

[2] Patent Number 5,114,477, granted May 19, 1992, based on Application 07/754,084, filed September 3, 1991. Assignor to Xerox Corporation, Stamford, Connecticut.

[3] Patent Number 5,188,918, granted February 23, 1993, based on Application 07/709,734, filed June 3, 1991. Assignor to Xerox Corporation, Stamford, Connecticut. (Ziolo II).

[4] Application 07/580,246, filed September 10, 1990. No Assignee of record.

Interference No. 103,281

Before METZ, SCHAFER and LEE, Administrative Patent Judges.

METZ, Administrative Patent Judge.

FINAL DECISION

The subject matter contested in this interference is directed to particular compounds which are a new, third form or allotrope of carbon known, variously, by their empirical formulae C_{60} or C_{70} and also known by the name fullerenes or so-called "Bucky Balls", and to pigment and toner compositions wherein the pigment or toner comprises a fullerene.

The specific interfering subject matter contested by the parties is defined by the sole count in this interference, Count 1, which is set forth below:

COUNT 1

Substantially pure solid C_{60} or C_{70}, or

a pigment composition comprising a fullerene, or

a toner composition comprising a fullerene.

The claims of the parties which correspond to Count 1 are:

Ziolo I:	Claims 1 through 6
Mort et al.:	Claims 1 through 21
Ziolo II:	Claims 1 through 18

Interference No. 103,281

Huffman et al.: Claims 45 through 77 and 79 through 180[5]

BACKGROUND

This interference was declared on December 2, 1993. On January 14, 1994, the junior party filed a paper captioned "EMERGENCY MOTION TO INVOKE THE SUPERVISORY AUTHORITY OF THE EXAMINER IN CHIEF OR THE BOARD OF PATENT APPEALS AND INTERFERENCES RE CLEARLY IMPROPERLY DECLARED INTERFERENCE" (Paper Number 8) wherein the junior party challenged the propriety of the declaration of this interference on various grounds. The senior party filed a paper captioned "RESPONSE TO EMERGENCY MOTION TO INVOKE THE SUPERVISORY AUTHORITY OF THE EXAMINER IN CHIEF OR THE BOARD OF PATENT APPEALS AND INTERFERENCES RE CLEARLY IMPROPERLY DECLARED INTERFERENCE; REQUEST FOR BIFURCATION AND IMMEDIATE RULING" (Paper Number 9). In an order mailed on February 16, 1994, the Administrative Patent Judge (APJ), in the

[5] Huffman et al. have proposed to cancel claims 52, 79, 82 and 87 from their involved application in order to "facilitate the analysis" of the issues presented (SB 16). Nevertheless, *ex parte* prosecution in an application involved in an interference is suspended upon declaration of the interference and amendments in the involved application will not be entered or even considered without the prior consent of the APJ. See 37 C.F.R. § 1.615 (a) and (b). Huffman et al. neither requested our consent to file an amendment canceling said claims nor filed a miscellaneous motion under 37 C.F.R. § 1.635 proposing to cancel said claims. We shall not grant our consent *nunc pro tunc*. Accordingly, claims 52, 79, 82 and 87, remain in Huffman et al.'s involved application and remain as claims designated as corresponding to Count 1.

performance of his interlocutory duties, informed the parties that Paper Numbers 8 and 9 would be treated jointly as a petition under 37 C.F.R. § 1.644(a)(3) and were thereafter forwarded to the Office of the Commissioner for a decision on the merits of the petition.

In the decision on the parties' petition, issued on March 21, 1994, all the relief sought by the parties in their petition was denied. Specifically, the decision noted at page 5:

> A review of the notice of declaration (Paper No. 2) and the records of the three patents and application involved in this interference, shows that the declaration is regular on its face.

With respect to the parties' contention that no claims of the parties were directed to "interfering subject matter", the decision further stated at page 5:

> Since the subject matter claimed by the parties facially appears to be related, it is not manifestly apparent at this stage of the interference that the parties are not claiming the same patentable invention within the meaning of 37 CFR § 1.601(n).

Thereafter, the it was specifically noted that the decision did not preclude the parties "from challenging the propriety of the interference in a motion or motions under 37 CFR § 1.633." (see page 6 of Paper Number 12). The decision concluded at page 11 by finding:

> This interference will most expeditiously proceed if all relevant issues are raised during the preliminary motion period.

After receiving the decision on petition, the parties filed various preliminary motions.

On June 8, 1995, this merits panel issued a decision on the parties' preliminary motions (Paper Number 38). Therein, we, *inter alia*, denied the motion for judgment on the grounds that the parties agreed there is no interference-in-fact; dismissed the junior party motion for immediate termination of the interference for lack of jurisdiction; dismissed a motion to substitute the count; denied the junior party motion to designate certain claims as not corresponding to the count; and, granted the senior party motion for benefit. We also placed the junior party under an order to show cause pursuant to 37 C.F.R. § 1.640(d)(3) and entered a *sua sponte* holding that all Huffman et al.'s claims corresponding to the count were directed to subject matter unpatentable under 35 U.S.C. § 101.

In denying the parties' motion for judgment on the grounds of no interference-in-fact, we performed the analysis required under 37 C.F.R. § 1.601(n) for determining whether or not the parties' claimed inventions were for the "same patentable invention" (see pages 4 through 6 of Paper Number 38). Specifically, we found that, assuming the junior parties' ink or toner composition claims were "prior art" with respect to the senior party, "the junior parties' toner compositions comprising C_{60} or C_{70} and the junior parties' ink composition comprising a

liquid vehicle and a fullerene would have anticipated (35 USC 102) or would have at least rendered obvious to a person of ordinary skill in the art (35 USC 103) the subject matter encompassed by the senior party's claims corresponding to the count." Alternatively, we found, assuming the senior party's claims to various fullerenes are "prior art" with respect to the junior parties' claims, the junior parties' toner and ink compositions would have been *prima facie* obvious to a person of ordinary skill in the art in light of age-old knowledge that carbon blacks are useful pigments or colorants for inks and toners.

We relied upon evidence in the nature of The Kirk-Othmer Encyclopedia of Chemical Technology, Volumes 11 and 15 (Second Edition, 1966), to support our conclusion that, at the time the junior party's applications which matured to become the involved patents in this interference were filed, carbon blacks would have been expected to be useful pigments or colorants. We also relied on Volume 6 of The Kirk-Othmer Encyclopedia of Chemical Technology (Third Edition, 1979) for the definition of the term "colorant". From all the above, we concluded that a person of ordinary skill in the art "would have expected fullerenes, an allotrope of elemental carbon derived from soot, in more or less pure form, to be useful colorants or pigments for inks or toners."

In response to the decision on motions, the junior party requested a final hearing to "review all the motions denied, dismissed, or rendered moot, including the Junior Party motions identified in the above Decision as 1), 2), 3) and 4)." (see Paper Number 40). In response to the *sua sponte* finding, the senior party filed a response contesting the basis for our finding on both procedural and substantive grounds (see Paper Number 46). The junior parties exercised their right to respond to the senior party's response to the *sua sponte* finding and filed a paper expressing their views on said finding (see Paper Number 51).

In Paper Number 56, we, *inter alia*, adhered to our *sua sponte* finding that all the claims of the senior party designated as corresponding to Count 1 were unpatentable and placed the senior party under an order to show cause pursuant to 37 C.F.R. § 1.640(d)(1). The senior party responded to the order to show cause by requesting a final hearing to review our *sua sponte* holding and other issues (Paper Number 58). In Paper Number 60, mailed December 18, 1996, we set forth the issues which would be reviewed at final hearing. Both parties filed briefs and the junior party filed a reply brief. A final hearing was held on May 20, 1998, which hearing was attended only by the senior party's legal representatives.

OPINION

Before we begin our analysis of the parties' respective positions on the issues before us, we note that the requirements for the parties' briefs are set forth in 37 CFR 1.656(b)(1) through 1.656(b)(8). Therein, the rules require, *inter alia*, citations to the "cases, statutes, other authorities and parts of the record" on which the parties rely to support the positions taken by them in their briefs. 37 CFR 1.656(b)(6). Moreover, 37 CFR 1.656(b)(5) requires:

> [a] statement of the facts, in numbered paragraphs, relevant to the issues presented for decision with appropriate references to the record (emphasis added)

Broad narratives by the parties in their briefs without specific citations to that portion of their record or exhibits which specifically support the positions taken by them in their briefs do not aid us in our resolution of the issues.

For example, the junior parties' position that certain motions concerning jurisdiction of this Board to decide the case before us and concerning whether or not there exists an interference-in-fact "were timely raised, are supported by both Partys [*sic*], were never decided, and are re-raised here" (JB 8)[6] is without basis in

[6] All reference to the junior parties' brief and reply brief are hereinafter referred to as "JB" and "JRB", respectively, followed by the relevant page numbers. The senior party's brief shall be hereinafter referred to as "SB" followed by the relevant page numbers.

the record. The senior party's representation that we have refused to address the issue of jurisdiction is also without factual basis and lacks merit (SB, page 12).

The senior party's continued argument (SB 3 through 5, 11, 30, 34 and 39) that virtually all research in the field of fullerenes conducted after they developed their process for preparing fullerenes was enabled only because their process put fullerenes in the hands of researchers is also absolutely without foundation in the record. Mere reference to the various articles in this record dealing with the discovery and further characterization of fullerenes establishes that the various researchers used conventional, available analytical techniques in a substantial number of cases to identify and characterize fullerenes. The senior party has simply not directed us to evidence in the record which substantiates their mere argument. More importantly, the subject matter of Count 1 which defines the subject matter contested in this proceeding is not directed to a process for preparing fullerenes.

JURISDICTION

The junior parties argue that we have never decided the issue of jurisdiction of the Board and the senior party argues that we have refused to address the issue of jurisdiction. The arguments are misplaced since the parties do not dispute that when properly declared the Board has jurisdiction to conduct an interference proceeding, that the issue of whether the interference was properly

declared was submitted to the Commissioner via petition, and that the Commissioner has ruled that this interference was properly declared.

We do not sit to review the Commissioner's decision on petition. The parties' recourse would have lied in a civil action for a *writ of mandamus*.

INTERFERENCE-IN-FACT

After receiving the decision on petition (Paper Number 12), the parties availed themselves of the various relief suggested therein. Specifically, the parties filed various preliminary motions, including a motion for judgment under 37 C.F.R. § 1.633(b) on the grounds that there was no interference-in-fact (see Paper Numbers 17 and 33). In Paper Number 38, this merits panel rendered its decision on the various preliminary motions filed by the parties, including the motion for no interference-in-fact, which was denied.

In denying the motion under 37 C.F.R. § 1.633(b), we set forth the proper test for determining whether an interference-in-fact exists. Specifically, we noted that when two or more parties had one or more allowable claims in their respective patents or applications which were directed to the "same patentable invention" as the claims of another party, an interference-in-fact existed. Stated another way, we found that it was by comparing the parties' various claims not the count, which determined whether or not an interference-in-fact existed. Thereafter, we went through specific, step-by-step

analysis according to the rules and analyzed the parties' various claims designated as corresponding to the count. We found that:

> it is apparent that the parties are claiming the "same patentable invention" in the sense of 37 CFR 1.601(n). Specifically, assuming that the junior parties' ink or toner compositions are "prior art" with respect to the senior party's claims corresponding to the count, the junior parties' toner compositions comprising C_{60} or C_{70} and the junior parties' ink composition comprising a liquid vehicle and a fullerene would have anticipated (35 USC 102) or would have at least rendered obvious to a person of ordinary skill in the art (35 USC 103) the subject matter encompassed by the senior party's claims corresponding to the count.
>
> Alternatively, assuming the senior party's claims to various fullerenes are "prior art" with respect to the junior parties' claims, the junior parties' toner and ink compositions would have been *prima facie* obvious to a person of ordinary skill in the art in light of age-old knowledge that carbon blacks are useful pigments or colorants for inks and toners. See, for example, The Kirk-Othmer Encyclopedia of Chemical Technology, Volume 11, "Inks" (Second Edition, 1966), wherein it is disclosed at page 611 that:
>
> > Printing ink is a mixture of coloring matter dispersed or dissolved in a vehicle or carrier, which forms a fluid or paste which can be printed on a substrate and dried. The colorants used are generally pigments, toners, and dyes, or combinations of these materials, which are selected to provide color contrast with the background on which the ink is printed.
>
> and at page 631 that:

> The electrostatic ink, also called an electrostatic toner, is a powder composed of pigment dispersed in a resin.

A "colorant" is described at page 529 in Volume 6 of The Kirk-Othmer Encyclopedia of Chemical Technology (Third Edition, 1979) as a substance "added to materials to produce color effects" and that such substances are usually classified as "dyes (qv) or pigments (qv)." Finally, in Volume 15 of the Second Edition of Kirk-Othmer, at page 542, the principal black pigments are described as "those which consist of elemental carbon in a more or less pure form" and include carbon blacks and lampblacks. Thus, we consider that a person possessing ordinary skill in the art would have expected fullerenes, an allotrope of elemental carbon derived from soot, in more or less pure form, to be useful colorants or pigments for inks or toners. Indeed, during the prosecution of the senior party's involved application in this interference and in response to the examiner's allegation that the fullerenes possessed no known utility, the senior party presented a declaration including as an exhibit drawings by one of the inventors which were "paintings" made by using fullerenes as the pigment in a carrier (see Paper Number 17). Accordingly, we agree with the primary examiner's determination that the claims of the junior parties and the claims of the senior party designated as corresponding to the count define the "same patentable invention" in the sense of 37 CFR 1.601(n).

Rather than address our analysis and the specific underlying findings which served as the factual basis for our conclusions, the parties focus on facts and theories which are not relevant to the issue before us. For example, the junior parties argue that: because the parties agree that there is no interference-

in-fact, there is no interference-in-fact and this interference should not have been declared (JB 19); because the senior party never claimed nor ever intended to claim inks or toners including fullerenes there was never any basis for declaring this interference (JB 20, 22); the senior party's claims designated as corresponding to the count include claims which were under rejection and should not have been included in the interference (JB 14, 21); and, the count in this interference is an improper and unpatentable count (JB 21, 22).

The senior party repeats its contention that it agrees with the junior party that there is no interference-in-fact between the parties (SB 59). The senior party also challenges our analysis from our decision on motions on the grounds that the evidence on which we relied does not establish the equivalence of "carbon black" with fullerenes (SB 61). Additionally, the senior party urges without explaining the factual basis for their position that, even assuming the junior parties' claims to inks or toners comprising fullerenes were prior art, there was no basis for our conclusion that the junior parties' claims would have anticipated or at least rendered obvious the claims to fullerenes, *per se* (SB 62).

As we found in our decision on motions and, indeed, as the parties were informed in Paper Number 12 (see page 5 of Paper Number 12), the fact that the parties agree that there is no interference-in-fact is neither controlling nor binding on the PTO. See Hsing v. Myers, 2 USPQ2d 1861, 1863 (BPAI 1987) (PTO not bound by parties'

stipulation that no interference-in-fact exists) (citing Jones v. Stuart, 192 USPQ 475 (Comm'r Pats. 1975)). Rather, whether or not an interference-in-fact exists is a question of fact and requires a comparison of the parties' claims to determine if any of the parties' claims are directed to the "same patentable invention" in the sense of 37 C.F.R. § 1.601(n). The junior parties' continued argument concerning the allegedly improper count in this interference is irrelevant to the question of whether or not an interference-in-fact exists. As noted on page 7 of Paper Number 12:

> The focus of a preliminary motion under § 1.633(b) is not on the count, but on the respective claims of the parties. Thus, a preliminary motion under § 1.633(b) is not logically inconsistent with the alternative format of the count.

Neither party has explained in their respective briefs the basis for their argument, *vis-à-vis* 37 C.F.R. § 1.601(n), that no claim of either party is directed to the "same patentable invention".

Similarly, the parties' argument that there is no interference-in-fact because no party has a claim identical to a claim of their opponent evidences a misunderstanding of the applicable law. As noted on page 9 of Paper Number 12:

> the declaration of an interference is not dependent on a "conclusion of identic invention." Under the regulations, an interference may be declared when the parties have claims drawn to the "same patentable invention." 37 CFR § 1.601(i). See also Aelony v. Arni, 547 F.2d at 570, 192 USPQ at 490.

While the senior party again agrees with the junior parties that "there is no interference-in-fact" (SB 59), as observed on page 9 of Paper Number 12 this position is inconsistent with the senior party's concession that "the pigment and toner compositions including fullerenes are obvious in view of the fullerene product." It is equally inconsistent with the senior party's position that the proper procedure would have been to issue the senior party's application and then have the Commissioner order a reexamination (37 C.F.R. § 1.520) of the junior parties' patents using the senior party's issued patent as "prior art" (SB 58).

The junior parties' argument that the senior party has no claims to toners or inks comprising fullerenes ignores all that we have stated above with respect to the proper analysis for determining whether or not an interference-in-fact exists. We repeat that it is not necessary for parties to have identical claims in order to support a conclusion that an interference-in-fact exists. Rather, it is only necessary that the parties have in their respective patents and application a single allowable claim directed to the "same patentable invention" as defined in 37 C.F.R § 1.601(n). See Conservolite Inc at 21 F.3d 1101, 30 USPQ2d at 1628, wherein the court noted: "The current rules do not require "copying" claims."

In our decision on motions we set forth our reasoning and analysis for concluding that there is an interference-in-fact between the parties. The junior parties' briefs completely ignore that

reasoning and analysis. Thus, we are not persuaded of any reason for changing our decision below, which decision we adopt and to which opinion we herein adhere.

We recognize that Huffman et al.'s claims 45 through 77, 79 through 84, 86 through 89, 91 through 93 and 96 through 180 have been indicated by the examiner in the Interference - Initial Memorandum as corresponding to the count and not allowable. Nevertheless, claims 85, 90, 94 and 95 are designated as corresponding to the count and allowable. As we stated above, it is only necessary that the parties have in their respective patents and application at least one claim which is allowable and directed to the "same patentable invention" in order to support a finding that there is an interference-in-fact and to declare an interference. After the termination of this proceeding by the issuance of a judgment and upon return to the examining group of the senior party's involved application, prosecution will be re-opened and the issues which formed the basis for the examiner's determination that the senior party's claims were unpatentable must be resolved before the examiner. Suffice it to say, the junior parties failed to move for judgment against the senior party under 37 C.F.R. § 1.633 on any grounds let alone the grounds which form the basis of the rejections made by the examiner below.

The senior party contends that we failed to set forth our rationale for concluding that, assuming the junior parties' ink or toner compositions were "prior art" with respect to the senior party's claims corresponding to the count, the junior parties' toner

compositions comprising C_{60} or C_{70} and the junior parties' ink composition comprising a liquid vehicle and a fullerene would have anticipated (35 USC 102) or would have at least rendered obvious to a person of ordinary skill in the art (35 USC 103) the subject matter encompassed by the senior party's claims corresponding to the count (SB 62). The senior party's contention lacks any reference to any facts in the record which supports their contention. Indeed, the record contains evidence to the contrary.

It was our position and remains our position that a claim directed to "C_{60}" is anticipated by a claim to "a toner comprising C_{60}", assuming the toner claim is prior art with respect to the claim to C_{60} because the toner claim "describes", in the sense of 35 U.S.C. § 102, the claim to C_{60}. Because anticipation has been held to be the "epitome" of obviousness, the toner claim also would have at least rendered obvious the claim to C_{60}. We also disagree with Huffman et al.'s argument at page 61 of their brief that "there is nothing in the record which permits the Board to equate "carbon black" with fullerenes." In the first instance, our finding that the toner claims comprising C_{60} anticipated the claims to C_{60} was adequate to support our conclusion that there was an interference-in-fact. Further, Huffman et al. mischaracterize what we held in our decision on motions. Specifically, taken in context, after the *Kirk-Othmer Encyclopedia of Chemical Technology* to support our conclusions, we said at pages 4 through 6 of Paper Number 38:

> the junior parties' toner and ink compositions would have been *prima facie* obvious to a person of ordinary skill in the art in light of age-old knowledge that carbon blacks are useful pigments or colorants for inks and toners. .... the principal black pigments are described as "those which consist of elemental carbon in a more or less pure form" and include carbon blacks and lampblacks. .... Thus, we consider that a person possessing ordinary skill in the art would have expected fullerenes, an allotrope of elemental carbon derived from soot, in more or less pure form, to be useful colorants or pigments for inks or toners.

Still further, Huffman et al.'s process produces what is described by them as "a sooty carbon product which is graphitic carbon including a few percent of C_{60} and low levels of C_{70} which are recoverable." (see page 2, lines 22 through 24 of Huffman et al.'s specification). Thus, to the extent Huffman et al.'s claims embrace the product produced by their process, it includes graphitic soot (a carbon black) which includes "a few percent of C_{60}". Carbon blacks are notoriously well-known pigments for toners and C_{60} has been found in commercial carbon blacks. See the article by Shigamatsu attached to Paper Number 56, for example.

THE DESIGNATION OF THE JUNIOR PARTIES' CLAIMS

The junior parties, having had their motion filed pursuant to 37 C.F.R. § 1.633(c)(4) to redefine the interference to change the designation of certain of their claims originally designated as corresponding to the count to claims not corresponding to the count denied (see Paper Number 38), maintain in their main brief that

various claims of their U.S. Patent Numbers 5,188,918, 5,114,477 and 5,232,810 are separately patentable from the subject matter of the count and should, therefore, have been designated as not corresponding to the count. The senior party urges us to reject the junior parties' various positions on this issue because the senior party believes the junior parties' evidence, such as it is, is inadequate to meet the junior parties' burden of proof. Additionally, the senior party urges us to reject the junior parties' arguments that: (1) a method of using a material is, *per se*, separately patentable from the material itself; (2) the examiners who issued the junior parties' patents found the junior parties' claims to be separately patentable from the fullerenes, *per se*; (3) the senior party application does not support the junior parties' claims designated as corresponding to the count.

In our decision on motions, we denied the junior parties' motion because the junior parties had not met their burden of persuasion and overcome the rebuttable presumption that claims originally designated as corresponding to the count are directed to the "same patentable invention" in the sense of 37 CFR 1.601(n) (page 12 of Paper Number 38). We found that the junior parties had failed to establish the separate patentability of their claims by making a claim-by-claim comparison of each of their claims designated as corresponding to the count with each of the other parties' claims designated as corresponding to the count whose designation was not

disputed (*Id.*). Stated in terms of the requirements of 37 C.F.R. § 1.637(c)(4), the junior parties' motion failed to "[s]how that the claim does not define the same patentable invention as any other claim whose designation in the notice declaring the interference as corresponding to the count the party does not dispute."[7] We also agreed with the senior party that none of the evidence submitted by the junior parties with their motion addressed the issue of whether or not the claims sought to be "undesignated" were separately patentable from all the other claims designated as corresponding to the count (*Id.*).

Rather than address our reasons for denying the motion below, the junior parties re-present the same arguments and rely on the same evidence which we found to be lacking below. We have carefully reconsidered our decision as set forth in Paper Number 38 but, except for our *sua sponte* determination with respect to Ziolo I's claims 1 through 6 set forth below, we remain unpersuaded by any of the arguments made by the junior parties in their brief that we erred in reaching our decision.

Nevertheless, in spite of our conclusion that the junior parties have not met their burden of persuasion concerning the denial of their motion, we have reconsidered our conclusion to the extent we held that Ziolo I's claims 1 through 6 directed to toners where the fullerene is used as a charge stabilizing agent are directed to the

[7] 37 C.F.R. § 1.637. 1995.

"same patentable invention" as the claims of any other party designated as corresponding to Count 1. Accordingly, pursuant to our express authority under 37 C.F.R. § 1.655(c), we shall, *sua sponte*, grant-in-part the junior parties' motion (Paper Number 20) to the extent the relief sought is a finding that claims 1 through 6 of Ziolo I (U.S. Patent Number 5,232,810) do not correspond to Count 1.

The claims of Ziolo I are directed to toner compositions comprising resin particles, pigment particles and a charge enhancing additive "comprised of a fullerene or fullerenes wherein the fullerene or fullerenes are comprised of C_{60} carbon, C_{70} carbon, C_{84} carbon, C_{234} carbon, C_{340} carbon, or mixtures thereof." While Ziolo I also contemplates the use of fullerenes as pigments for the claimed toner compositions (see column 6, lines 25 through 36) and while we adhere to our position as expressed above concerning why the use of fullerenes as a pigment would have been obvious in the sense of 35 U.S.C. §103, there is no evidence in this record which establishes that fullerenes, *per se*, were known as charge enhancing additives in toner compositions. There is also no evidence in this record which establishes why fullerenes would have been expected to have properties which would have made them useful as charge enhancing agents in toners. We know of no independent reason why it would have been expected that fullerenes, a third allotrope of carbon, would have been expected from its properties to have been a useful charge enhancing agent. Therefore, assuming the claims of the parties

designated as corresponding to the count were prior art with respect to claims 1 through 6 of Ziolo I, none of those claims would have anticipated or rendered obvious Ziolo I's claims 1 through 6.

Accordingly, this interference will be redeclared in a separate paper filed on even date with this decision to reflect that claims 1 through 6 of Ziolo I do not correspond to Count 1.

THE PATENTABILITY OF THE SENIOR PARTY'S CLAIMS

We first raised the issue of whether or not the senior party's claims designated as corresponding to Count 1 are patentable in our decision on motions. Therein, we *sua sponte* found that:

> the article by Buseck et al. in Volume 257 of the July 1992 Science magazine and the Hecht article in the March 1994 New Scientist magazine to be evidence that fullerenes, in the form of C_{60} and C_{70}, are naturally occurring forms of carbon found in nature in the strata of certain Precambrian rocks (shungite) and Cretaceous period clays, albeit in infinitesimal amounts. In our view, Huffman et al.'s claims corresponding to the count do not exclude or distinguish from the naturally occurring fullerenes. Specifically, there is no evidence in the record which establishes that Huffman et al.'s C_{60} and C_{70} differs in form, quality or properties from naturally occurring C_{60} and C_{70}.

We subsequently afforded the parties an opportunity to respond to our *sua sponte* finding. After considering the parties' responses to the *sua sponte* holding we adhered to our conclusion that the senior party's claims designated as corresponding to Count 1 were unpatentable under 35 U.S.C. § 101 on the grounds that:

> C_{60} and C_{70} are naturally occurring substances and Huffman et al.'s claims either read on the naturally occurring fullerenes or do not exclude the naturally occurring fullerenes.

An order to show cause was issued against the senior party and we also cited therein additional references which established the existence of fullerenes on earth in geological strata (see Paper Number 56). The senior party responded, *inter alia*, by requesting a final hearing to review our decision.

The basis for our *sua sponte* finding was the evidence in the nature of the various publications we cited which established that C_{60} and C_{70} were found, naturally, in the earth's crust in various geological strata in various locations around the earth. As we stated in the order to show cause of September 5, 1996:

> our holding was founded on the dual footing that C_{60} and C_{70} are naturally occurring substances and Huffman et al.'s claims either read on the naturally occurring fullerenes or do not exclude the naturally occurring fullerenes. There is no persuasive objective evidence in the record which establishes that Huffman et al.'s claimed C_{60} and C_{70} differ from the naturally occurring fullerenes "in form, quality or substance". In short, our *sua sponte* holding was and is based on the fact that Huffman et al.'s claims corresponding to the count encompass naturally occurring fullerenes and that naturally occurring fullerenes are not "new" in the sense used in 35 USC 101.

Based on the aforementioned articles and the award for the 1996 Noble Prize in chemistry to Smalley, Curl and Kroto, three of the five authors of the 1985 Nature article on which we relied as part of the

evidence that fullerenes existed in natural form in nature, we further informed the parties that we could not, assuming the senior party prevailed in this proceeding, award judgment to the senior party with respect to certain claims which represented or included the discovery of Smalley et al.

The junior party urges us to sustain our determination that the senior party's claims designated as corresponding to Count 1 are unpatentable. The junior party urges that the senior party's claims are unpatentable under 35 U.S.C. § 101, for reasons raised by us in our various decisions below; and are unpatentable under 35 U.S.C. §§ 102, 103 and 112, for reasons raised by the examiner during *ex parte* prosecution of the Huffman et al. application involved in this interference; and, for various reasons raised before the European Patent Office. Contrariwise, the senior party urges that we should reverse our decisions below and find the senior party's claims patentable because they are not the same as the products of nature alleged by us to have been established in the various articles on which we relied. Moreover, the senior party now directs us to specific limitations in specific claims or groups of claims which allegedly distinguish from and exclude the fullerenes found in the earth's crust (SB 17 through 21).

In light of the junior parties' arguments, we believe it necessary to state here what did not form the basis of our *sua sponte*

finding. We stated in the order to show cause of September 5, 1996, our holding was:

> based on the fact that Huffman et al.'s claims corresponding to the count encompass naturally occurring fullerenes and that naturally occurring fullerenes are not "new" in the sense used in 35 USC 101.

We were not then and are not now suggesting that any claim of Huffman et al. corresponding to Count 1 is unpatentable based on any "prior art" as defined in 35 U.S.C. § 102, under either 35 U.S.C. §§ 102 or 103. Rather, in Paper Number 56 at page 17 in response to Huffman et al.'s argument that the articles on which we relied were not "prior art" because their publication date was subsequent to Huffman et al.'s effective filing date, we stated:

> we did not rely on these articles as "prior art" as defined in 35 USC 102 under either 35 USC 102 or 35 USC 103 but instead relied on these articles as evidence of the fact that fullerenes occurred naturally in deposits in the earth's crust prior to Huffman et al.'s filing date and, as such, were ineligible for patent protection under 35 USC 101 based on the Supreme Court's decision in Diamond v. Chakrabarty, 447 U.S. 303, 100 S.Ct. 2204, 206 USPQ 193 (1980). Reliance on such references to show a state of fact has been upheld by the predecessor to our reviewing court. In re Langer, 503 F.2d 1380, 1391, 183 USPQ 288, 297 (CCPA 1974); In re Wilson, 311 F.2d 266, 268, 135 USPQ 442, 444 (CCPA 1962).

We remain convinced that the articles on which we relied prove by a preponderance of the evidence that C_{60} and C_{70} are found in various geological strata in different locations around the earth. Additionally, we cited other articles in the Order to Show Cause

which further substantiated that fullerenes are old compounds found in geological strata in Canada and Russia and also found in various types of carbon blacks. Because all the articles on which we relied speak in terms of the empirical formulae C_{60} and C_{70} in referring to fullerenes and because we presume that the empirical formulae must describe the particular geometry now understood to represent the soccerball-like structure of fullerenes, we reject Huffman et al.'s mere argument that fullerenes are not found in the earth's crust. Stated another way, Huffman et al. have failed to establish that the formulae C_{60} and C_{70} by which the various articles refer to fullerenes may represent some compound other than the fullerenes which Huffman et al. claim. Accordingly, we reject Huffman et al.'s mere hypothesis that naturally occurring fullerenes are not found in nature in a "3 dimensional array". Indeed, the first sentence from the article which is Exhibit 7 to the Kroto declaration states:

> Naturally occurring fullerenes have been found in rock samples that were subject to singular geologic events such as lightening strikes (1), wildfires at the K-T boundary (2) and meteoritic impacts (3). [emphasis added].

Additionally, at page 127 of the Kroto article which is Exhibit 3 to the Kroto declaration, the author, Harold W. Kroto, concludes that:

> Now we have discovered that an unexpected molecule, C_{60}, has been under our noses on earth since time immemorial and was invisible until now. [emphasis added].

Accordingly, we do not consider the issue of whether or not C_{60} and C_{70} occur naturally or are found in deposits in the earth's crust to be open to serious question.

We also reject as lacking factual basis in the record Huffman et al.'s mere theory that the naturally occurring fullerenes exist as "molecules interspersed in the rocks in which they are alleged to be present" (SB 15). We also reject Huffman et al.'s mere argument that naturally occurring fullerenes are found in an impure state and are not crystalline. While the articles on which we have relied is silent on these properties, there is simply no evidence which supports any of Huffman et al.'s theories or argument. Rather, the narrow issue for us to decide is whether or not any of Huffman et al.'s claims designated as corresponding to Count 1 distinguish from the fullerenes (C_{60} and C_{70}) found in nature.

Huffman et al. do not concede the articles on which we relied prove the existence of fullerenes in the earth's crust. Nonetheless, Huffman et al. urge that their claims corresponding to the count may be considered in various groups as defined by particular claim language which language distinguishes them from C_{60} and C_{70} described in the articles on which we relied.

Specifically, Huffman et al. urge that claims 86, 96 through 108, 111 through 152 and 154 through 180 all require the fullerenes be present in "macroscopic amounts" which excludes the trace amounts of fullerenes as found in nature. It is argued that claims 84, 85, 89, 90, 94, 95, 102, 103 and 135 through 140 recite

that the fullerenes are "substantially pure" which is said to exclude the impure fullerenes found in nature. Huffman et al. also urge that claims 45 through 51, 73 through 75, 77, 80, 83, 85, 88, 90, 92 through 95, 111, 112 and 165 through 180 require either "solid" C_{60} or "solid" C_{70} which means the fullerenes can be seen unlike naturally occurring fullerenes which exist only in parts per billion (ppb) in nature in a one dimensional array. Claims 45 through 57 are said to distinguish from naturally occurring fullerenes by the use of the claim language "a solid consisting essentially of C_{60}, C_{70} or mixtures thereof." Under well-understood interpretation of the phrase "consisting essentially of", Huffman et al. urge that such claims exclude other materials found with the deposits of naturally occurring fullerenes. Claims 48 through 51, 73 through 75, 77, 92 through 95, 165 and 166 are said to distinguish from the naturally occurring fullerenes by reciting that the claimed fullerenes are "crystalline." Huffman et al. urge that their claims directed to a product-by-process (claims 119 through 132) distinguish from naturally occurring fullerenes because they are man made and because the products contain "macroscopic" amounts of fullerenes rather than mere trace amounts. Finally, it is argued that claim 86 recites a color for the product which "implies that the product is in macroscopic amounts" which distinguishes them from naturally occurring fullerenes.

We shall address the arguments by Huffman et al. by first analyzing the evidence on which we relied to reject Huffman et al.'s

claims and then interpreting the claims in their application, giving them their broadest, reasonable interpretation, consistent with the disclosure in Huffman et al.'s specification.

In our *sua sponte* holding we relied on the article by Buseck et al. in Volume 257 of the July 1992 Science magazine and the Hecht article in the March 1994 New Scientist magazine as evidence that fullerenes, in the form of C_{60} and C_{70}, are naturally occurring forms of carbon found in nature in the strata of certain Precambrian rocks (shungite) (Buseck et al.) and Cretaceous period clays (Hecht), albeit in infinitesimal amounts. In our order to show cause (Paper Number 56), we also cited six additional articles related to fullerenes. Four of the cited six additional references (Daly et al., Becker et al., Becker et al. and Buseck et al.) are directed to the presence of fullerenes in geological deposits found on earth. We find the two Becker et al. articles to be particularly relevant because they establish that fullerenes have been found in a rock formation known as the Sudbury impact structure in Ontario Canada which is 1.85 billion years old and are present in amounts of from 1 to 10 parts per million.

From all the above, we find it beyond argument that C_{60} and C_{70} are found in the earth's crust. Because there is absolutely no evidence in this record that C_{60} or C_{70} as referenced in the articles could represent any form of carbon other than the unique cage structure recognized for fullerenes, we find that fullerenes, or

bucky balls, are a form of carbon found naturally in the earth's crust.

"MACROSCOPIC AMOUNTS"

As our reviewing court noted in Markman v. Westview Instruments Inc., 52 F.3d 967, 980, 34 USPQ2d 1321, 1330 (Fed. Cir. 1995) (*en banc*), *aff'd.*, 517 U.S. 370, 38 USPQ2d 1461 (1996):

> As we have often stated, a patentee is free to be his own lexicographer. Autogiro, 384 F.2d at 397, 155 USPQ at 702. The caveat is that any special definition given to a word must be clearly defined in the specification. Intellicall, Inc. v. Phonometrics, Inc., 952 F.2d 1384, 1388, 21 USPQ2d 1383, 1386 (Fed. Cir. 1992). The written description part of the specification itself does not delimit the right to exclude. That is the function and purpose of claims.

Accordingly, we begin our analysis of what the term "macroscopic" means by finding a definition of the term "macroscopic", *per se*, from several dictionaries for the purpose of establishing the plain and ordinary meaning of the word "macroscopic". The first definition of "macroscopic" in "Webster's Third New International Dictionary of the English Language" is:

> large enough to be observed by the naked eye -- opposed to *microscopic*

"Hackh's Chemical Dictionary, Fourth Edition" defines macroscopic as:

> [d]escribing objects visible to the naked eye. *Cf. microscopic.*

Thus, the ordinary meaning of "macroscopic amount", in literal terms, is an amount visible to the naked eye, that is, visible without the

aid of a microscope. Unless Huffman et al. intended otherwise, we must give the term "macroscopic" its ordinary meaning.

Neither the involved Huffman et al. application nor its parent application, of which the involved application is a continuation-in-part and for which Huffman et al. were granted benefit, use the phrase "macroscopic" in *ipsimis verbis*. However, lack of *ipsimis verbis* support is not fatal to Huffman et al.'s use of the term in their claims.

No original claim in either the Huffman et al. benefit application or the involved application uses the term "macroscopic amounts". Rather, Huffman et al. amended claim 86 in the involved application in Paper Number 16 to change "measurable amount" to ---macroscopic amount---, and added new claims 96 through 185, some of which new claims included the phrase "macroscopic amounts". Huffman et al. argued in their amendment that the new terminology found support in their original disclosure and urged that their claims as amended and the newly added claims were patentable (see Paper Number 16 beginning in the paragraph bridging pages 10 and 11 and concluding on page 12 in the third full paragraph).

At page 1, lines 25 through 30 of their specification, Huffman et al., in discussing the prior art, state that:

> Yet, to date, no one has been successful in verifying the existence of this molecule since no one has been successful in isolating the molecule <u>in measurable amounts</u>. Thus, no process for producing

> recoverable amounts of this new compound have been described. (emphasis added).

In the first instance, we do not consider, and Huffman et al. have not established on this record, either that "no one has been successful in isolating the molecule in measurable amounts" or that "no process for producing recoverable amounts of this new compound have been described." We find no nexus between the term "macroscopic amount" and "measurable amounts" or "recoverable amounts". Certainly, a microscopic amount of a product is capable either of being recovered or measured by any number of well-known techniques.

Huffman et al.'s specification, at page 2, lines 17 and 18, describes their process as enabling the "production of recoverable amounts of C_{60} and C_{70}." At lines 22 through 24 of page 2, Huffman et al. describe the product prepared by their process as:

> a sooty carbon product which is graphitic carbon including a few percent of C_{60} and low levels of C_{70} which are recoverable from the product.

We find this disclosure to mean that from an unidentified amount of "graphitic carbon" produced by their process, Huffman et al. obtain a small amount of, but more than 1 (one) percent of, C_{60} and even less C_{70}, based on the amount of "graphitic carbon" obtained. Whether or not such amounts of C_{60} and C_{70} are "macroscopic" cannot be determined from this disclosure alone.

On page 3 of the specification, 4 (four) figures of drawing are described. Figure 1 is said to be "a micrograph of typical crystals of the 98% C_{60}, 2% C_{70} material showing thin platelets, rods

and stars of hexagonal symmetry." The reference to "typical crystals of the 98% C_{60}, 2% C_{70} material" is not further explained or described and we cannot ascertain to what specific material Huffman et al. is referring. Figure 2 is described as an "X-ray diffraction of a microcrystalline powder of the 98% C_{60}, 2% C_{70} solid material." Again, what specific material is being referenced cannot be determined. Figure 3 is described as an infrared (IR) absorption spectrum of a 2 (two) micrometer thick coating of the fullerene mixture described in the previous figures on a silicon substrate. Figure 4 is a visible-ultraviolet absorption spectrum of a 0.1 micrometer coating of the aforementioned fullerene mixture on quartz.

On page 7, lines 2 through 10 of their specification, Huffman et al. describe how they obtain fullerenes by vaporizing graphite. Specifically, they state therein that:

> [t]he electrical heating vaporizes the constricted tip of the graphite rod producing a high density vapor of carbon, which quickly condenses into smoke consisting of very fine particles (of the order of 0.1 microns) of graphitic carbon with an admixture of a few percent of the desired C_{60} molecule. [emphasis added]

We take official notice that the human eye cannot detect a particle 0.1 micron in size without the aid of a microscope. Thereafter, on page 8 of the specification, Huffman et al. reference Figure 1 in discussing their "[s]tudies by optical microscopy of the C_{60} material which is left after evaporating the benzene solution". We believe it is plain from this disclosure that the product of Figure 1 requires a

microscope to be seen and is not "macroscopic" because the product cannot be seen with the naked eye. The further discussion on page 8 of the X-ray diffraction studies conducted by Huffman et al. on the product obtained by them using their process with its reference to individual crystals does nothing to clarify the meaning of "macroscopic" as used by Huffman et al. Indeed, in Huffman et al. Exhibit 3 (the videotape), the observation of the evaporation of solvent with subsequent formation of crystals is observed with a microscope! Thus, it would appear that individual crystals are not visible to the naked eye and, therefore, are not "macroscopic" in the ordinary sense.

On page 11 of their specification, Huffman et al. discuss films or coatings of C_{60} as comprising "sub-micron microcrystalline particles of solid C_{60}". Beginning in the paragraph bridging pages 11 and 12 and continuing on page 12, Huffman et al. discuss the IR spectrum of "an approximately 2 micrometer thick coating of C_{60} coating on a silicon substrate." Suffice it to say that "sub-micron" particles and coatings several microns thick would not necessarily be expected to be visible to the naked eye. Thus, the microcrystalline particles of solid C_{60} and the 2 micrometer coating of the same cannot be said to be "macroscopic" in the ordinary sense of the term.

Example 1 on page 16 of the specification describes a "C_{60}-containing carbon dust" prepared by Huffman et al.'s process by evaporating graphite rods in a helium atmosphere of up to 400 torr. The product, carbon dust containing unidentified amounts of C_{60}, was

scraped from unidentified "substrates" and the internal surfaces of the reaction chamber. That product was worked-up by washing the dust with ether and subsequently extracting the previously ether-washed dust with benzene. Evaporation of the benzene solution yielded C_{60} as a "microcrystalline residue." It appears from Example 1 that the product obtained, a C_{60}-containing carbon dust", was visible to the naked eye because it could be scraped off the "substrates" and surfaces of the reaction chamber notwithstanding its description, after work-up, as a "microcrystalline residue". Thus, the "graphitic soot" obtained which contained an unidentified amount of C_{60} and even less C_{70} was visible.

In Example 2, the process of Example 1 is repeated but in helium at "2 or more atmospheres" (page 17 of the specification). The product obtained in Example 2 is said to contain "a greater percentage of C_{70} than does the product in Example 1." We find little or no description in this example which aids us in the resolution of what Huffman et al. mean by the claim language "macroscopic". Huffman et al. do suggest at page 2, lines 25 through 27 of their specification that increasing the pressure of inert gas (helium) increases "the fraction of C_{70} molecules" (emphasis added). Huffman et al. further disclose that while at higher pressures the ratio of C_{70}:C_{60} increases, the overall yield decreases (see page 4, line 16 through page 5, line 7 of the specification). Accordingly, for the reasons we expressed above with respect to Example 1, we find Example 2 to be of little assistance to us in understanding the

meaning we should give to the term "macroscopic" in Huffman et al.'s claims designated as corresponding to Count 1.

Example 3 on page 18 is described as a method for obtaining "[p]ure C_{60} and C_{70}". The method comprises dissolving the mixtures obtained from either Example 1 or 2 in benzene. The C_{60}- and C_{70}-containing benzene mixture is added to an alumina column for elution using benzene as the eluent. The fractions obtained are evaporated to dryness. Huffman et al. state that the presence of product in the fractions "can be determined by taking mass spectroscopy thereof." Because there is no yield data for the product obtained in either fraction, we find Example 3 does not shed much light on the meaning of "macroscopic" as utilized in Huffman et al.'s claims corresponding to Count 1.

From all the above, we find the term "macroscopic" is not, *per se*, defined anywhere in Huffman et al.'s disclosure in quantitative terms. However, because Huffman et al.'s disclosure as discussed above is not entirely inconsistent with the ordinary meaning of the term "macroscopic", we shall give said term its ordinary, well-accepted meaning of visible without the aid of a microscope or, simply, visible with the naked human eye.

In reaching this conclusion we have carefully considered the declaration of Kroto and the other evidence in this record. We find Kroto to be a recognized expert in this field. Indeed, he is one of the Nobel laureates credited with the discovery of fullerenes

by the Swedish National Academy in 1996. Kroto, like other researchers in this field as evidenced by numerous publications in the record, appears to acknowledge Huffman et al.'s contribution in this field to be their process for producing fullerenes in amounts not attainable before their invention. Nothing in Kroto's declaration, however, indicates that he was aware that Huffman et al. are claiming C_{60}, *per se*.

Nevertheless, we also conclude that the naturally occurring fullerenes described in the various references discussed above are not present in the earth's crust in "macroscopic" amounts because it would not be expected that amounts of up to 10 parts per million could be seen with the naked eye. Accordingly, to the extent the term "macroscopic amount" may be given its ordinary meaning, the claims using said term distinguish from the fullerenes found in the earth's crust which are not visible to the naked eye.

"SUBSTANTIALLY PURE"

Huffman et al.'s process, which process is no longer claimed by them in their involved application, does not produce "pure" C_{60} and/or C_{70} as argued by Huffman et al. Rather, their process produces an unquantified amount of carbonaceous soot from which small, further undefined amounts of "pure" C_{60} and/or C_{70} can be recovered and subsequently purified.

At page 2, lines 18 and 19 of their specification, Huffman et al. state that:

> A process has now been developed for the production of recoverable amounts of C_{60} and C_{70}.

At lines 22 through 24 of the same page, Huffman et al. continue by noting that:

> This process produces a sooty carbon product which is graphitic carbon including a few percent of C_{60} and low levels of C_{70}.

The process is described as pressure dependent. At page 4, lines 16 through 18, it is disclosed that:

> The amount of C_{60} and C_{70} produced from this carbon source is dependent upon the pressure of the quenching gas.

On page 7, lines 2 through 10 of their specification, Huffman et al. describe how they obtain fullerenes by vaporizing graphite. Specifically, they state therein that:

> [t]he electrical heating vaporizes the constricted tip of the graphite rod producing a high density vapor of carbon, which quickly condenses into a smoke consisting of very fine particles (of the order of 0.1 microns) of graphitic carbon with an admixture of a few percent of the desired C_{60} molecule. [emphasis added]

Additionally, at page 13, lines 26 through 31, Huffman et al. disclose that:

> Thus, using the procedures described hereinabove, at quenching pressures of less than 1 atmospheric pressure and especially at pressures of 50-400 torr, a product is produced which is predominantly C_{60} and contains minor amounts of C_{70}.

Recovery of the desired products from the sooty carbon product (graphitic carbon) is described at page 5, lines 18 through 26 of the specification wherein Huffman et al. teach that:

> The C_{60} and C_{70} molecules can be removed from this collected quenched product by contacting said quenched product with an extracting solvent. In other words, the black soot is placed in a container containing the extracting solvent, or the extracting solvent is poured onto the black soot placed in a container. In either case, the C_{60} and C_{70} molecules become dissolved in the solvent, while the remainder of the black soot remains insoluble.

Purification of the products so-recovered is described at pages 13 and 14 of the specification as being obtained by "conventional techniques known to one skilled in the art." Identification of the products prepared by the disclosed process is described at page 14, lines 26 through 29. Therein it is stated that:

> The fractions with product will contain microcrystals, the identity of which can be confirmed by spectroscopy, e.g., mass spectroscopy.

From all the above, we find the product of Huffman et al.'s process is graphitic carbon which contains a small but unquantified amount of C_{60} and even less C_{70}.

Nevertheless, we find that the various references on which we have relied to establish that C_{60} and C_{70} or fullerenes or bucky balls are found, naturally in the earth's crust, only establish that C_{60} and C_{70} are found in the earth's crust in large ore deposits and in amounts up to 10 parts per million (0.001 per cent). Based on the

articles on which we relied, we have not concluded that it would have been obvious to mine the fullerenes, separate them from the ore in which they are found and purify them. That would constitute a "prior art" rejection and, as we have stated, the statutory basis for our *sua sponte* was 35 U.S.C. § 101, on the grounds that C_{60} is not "new". Further, whether or not naturally occurring fullerenes, if recovered and purified, have the same properties as those claimed by Huffman et al. is not an issue before us. That is an issue for another forum. We simply note here that no reference on which we have relied to establish the prior existence of C_{60} and C_{70} in the earth's crust describes C_{60} and C_{70} to be present in graphitic soot. We also find that the evidence on which we relied to establish that fullerenes occur naturally in the earth's crust does not establish in what state of purity they are found. Accordingly, claims to "substantially pure" fullerenes are not barred under 35 U.S.C. § 101 by any of the articles on which we relied.

"SOLID CONSISTING ESSENTIALLY OF C_{60}"

Huffman et al. argue that the claims which recite that the fullerenes are a "solid" or a "solid consisting essentially of C_{60} or C_{70}" distinguish from the fullerenes found naturally in the earth's crust. Huffman et al. urge that the descriptive term "solid" means that "the product can be seen, consistent with usage in the art" (SB 18, footnote omitted). Moreover, Huffman et al. urge that because the articles on which we have relied only describe the fullerenes as

present in parts per billion that "presumptively only molecules are present." (SB 19). Huffman et al. additionally argue that when the term "solid" is further coupled with the language "consisting essentially of" the claims using said language even further distinguish from naturally occurring fullerenes because the geological formation containing the fullerenes "contains mostly other components and materials" (page 19 of their brief).

We find little merit in Huffman et al.'s mere argument that the term "solid" distinguishes Huffman et al.'s claims from naturally occurring fullerenes. In the first instance, Huffman et al. have supplied absolutely no evidence to support their implied argument that naturally occurring fullerenes are not solid or lack definite shape and volume. Neither have Huffman et al. furnished any evidence which substantiates that naturally occurring fullerenes, because they cannot be seen with the naked eye, are not solids. We take the articles on which we relied on their face as establishing that carbon, in the form of C_{60} and C_{70}, has been found in the earth's crust and that such deposits are ancient. Indeed, this very disclosure formed the basis for our conclusion that C_{60} and C_{70} were not "new" in the sense of 35 U.S.C. § 101.

Huffman et al. have provided no meaningful scientific basis or any evidence for concluding that the C_{60} identified in the articles exists in a different state of matter than the C_{60} which they prepared by vaporizing a graphite rod. Indeed, as we have stated above, we find that the empirical formula C_{60} necessarily

defines the unique soccerball-like structure that Smalley et al. determined to exist in their seminal paper on this matter.

The phrase "consisting essentially of" is judicially recognized as rendering the claim open for the inclusion of unspecified ingredients which do not materially affect the basic and novel characteristics of the composition. In re Herz, 537 F.2d 549, 551 [1,2], 190 USPQ 461, 463 [1] (CCPA 1976); In re Janakirama-Rao, 317 F.2d 951, 137 USPQ 893 (CCPA 1968).

In Janakirama-Rao at 317 F.2d 954, 137 USPQ 896, the court specifically noted that:

> [t]he word "essentially" opens the claims to the inclusion of ingredients which would *not* materially affect the *basic* and *novel* characteristics of appellant's compositions as defined in the **balance** of the claim, according to the applicable law. [emphasis on "balance" added].

Further, in discussing Herz's specification with respect to Herz's composition's novel antioxidant properties vis-à-vis the prior art (Messina), the court in Herz at 537 F.2d 552 [4], 190 USPQ 463, concluded that:

> Appellants' specification states that the composition can contain any of the well-known additives, including dispersants. There is no evidence that Messina's dispersant would materially affect the basic and novel characteristic of their composition, and all evidence is to the contrary. Messina's composition has the same basic and novel characteristic - increased oxidation resistance - although it has additional enhanced detergent-dispersant qualities. (underlining added).

Thus, we must look to Huffman et al.'s disclosure to first determine what is the nature of the product obtained by their process for the purpose of interpreting the meaning of "consisting essentially of" in Huffman et al.'s claims.

As we stated above, the Huffman et al. process prepares a mixture described by them as "a sooty carbon product which is graphitic carbon containing a few percent of C_{60} and low levels of C_{70}." Thus, Huffman et al.'s product obtained by their process but before purification is predominantly graphitic carbon soot which includes "a few per cent" of C_{60} and less C_{70}. Because a product which is predominantly graphitic soot would be expected to have the properties of graphitic soot and not the properties of the "few percent" of fullerenes included in said soot, we find the language "consisting essentially of" excludes the graphitic soot containing fullerenes described by Huffman et al. but not the fullerenes isolated and recovered from said graphitic soot. Accordingly, we interpret the claims using the partially closed claim language "consisting essentially of" as claims to isolated and substantially purified C_{60}. Accordingly, the language "a solid consisting essentially of C_{60}" describes a product which is not shown in any of the references on which we have relied to be found naturally in deposits on the earth.

"CRYSTALLINE"

The Huffman et al. disclosure makes numerous references to: "crystals" of C_{60} and C_{70}; obtaining product from graphitic soot by

"crystallization"; and, the description of the "crystals" observed by optical microscopy as "what appear to be rods, platelets, and star-like flakes". Nonetheless, the specific claim term "crystalline" is not defined by Huffman et al. Accordingly, we shall give the claim term its ordinary meaning, considered in light of Huffman et al.'s disclosure but without importing limitations from the disclosure into the claims.

Claims 52 and 79 of Huffman et al.'s application designated as corresponding to Count 1 are directed to either "amorphous" or "crystalline" solid which exhibit or have certain physical properties. Because these claims require in the alternative that the claimed materials can be crystalline, we shall consider them here.

Huffman et al. urge that the claims which describe the fullerenes as "crystalline" are patentable because crystallinity is, allegedly, "another characteristic of C_{60} and/or C_{70} not naturally found" (see page 19 of their brief). We are directed to claim 48 among others, which is said to include this limitation. Nevertheless, claim 48 does not recite the term "crystalline" but only recites "A solid consisting essentially of C_{60}." Thus, Huffman et al.'s arguments are unpersuasive with respect to claim 48.

With respect to the remaining claims said to include this limitation, we are not persuaded by Huffman et al.'s mere arguments that the naturally occurring fullerenes are not necessarily "crystalline". As we stated above, we find that the compound denoted by the empirical formula C_{60} necessarily describes the soccerball-

shaped molecule come to be known as a fullerene. Huffman et al. have provided no evidence that C_{60} denotes any other molecule or that C_{60} exists in any other form. By definition, crystallinity describes a particularly arranged or ordered structure as opposed to a random orientation or no orientation. However, whether the specific shape of the fullerene molecule found naturally in the earth's is crystalline or amorphous is not set forth in any of the articles on which we have relied as evidence that fullerenes are naturally occurring materials. Accordingly, the language "crystalline" used to further describe the subject matter claimed by Huffman et al. distinguishes from naturally occurring C_{60} as described in the articles on which we have relied as a bar under 35 U.S.C. § 101.

"PRODUCT-BY-PROCESS"

Huffman et al. urge that their claims directed to a product-by-process are distinct from and therefore patentable from the naturally occurring fullerenes found in the earth's crust. Huffman et al. emphasize that their fullerenes are synthetically produced, unlike the naturally occurring fullerenes. Huffman et al. stress that the fullerenes obtained from their sooty carbon product do not contain trace amounts of fullerenes but macroscopic amounts which further distinguish from the naturally occurring fullerenes. Finally, Huffman et al. urge that based on the Kroto declaration it is established that their sooty carbon product is different from natural soot found in nature.

It is well-understood that, even though product-by-process claims are defined by the process in which they are made, determination of their patentability is based on the product itself. In re Thorpe, 777 F.2d 695, 227 USPQ 964 (Fed. Cir. 1985). As the court stated in Thorpe, 777 F.2d at 697, 227 USPQ at 966:

> The patentability of a product does not depend on its method of production. In re Pilkington, 411 F.2d 1345, 1348, 162 USPQ 145, 147 (CCPA 1969). If the product in a product-by-process claim is the same as or obvious from a product of the prior art, the claim is unpatentable even though the prior product was made by a different process. (citations omitted).

Although we are not here presented with patentability in the sense of 35 U.S.C. §§ 102 and 103, to be patentable under 35 U.S.C. § 101, Huffman et al.'s product must be shown to differ in form, quality or properties from naturally occurring C_{60} and C_{70}.

Huffman et al. urge that their product-by-process claims not only define a particular product in terms of its crystallinity, color and shape, all qualitative properties, but also that Huffman et al.'s product-by-process claims define their product in quantitative terms, that is, that the claims also define "macroscopic" amounts of their particular product. Nevertheless, Huffman et al.'s claims to product-by-process use various terms to define them and are therefore of varying scope.

Claim 53 recites a product produced by a five-step process including the preparation of a sooty carbon product with subsequent recovery of a "solid carbon product comprising C_{60} molecules." Claims 70 and 71, further modify the subject matter of claim 53 by

identifying the product of the process as also "further comprising C_{70}" (claim 70) and by reciting a further purification step of the C_{60} molecules to "obtain C_{60}" (claim 71). Claims 108 through 110 recite various limitations to the "C_{60} molecules" obtained by the process of claim 53.

Claim 119 recites a product prepared by a two-step process to obtain a "sooty carbon product comprising C_{60} molecules" in an amount sufficient "to allow macroscopic amounts of C_{60} to be separated from said soot." Claim 141 describes a product prepared by a process including a sublimation step to recover a "carbon product comprising C_{60}." Claim 155 further provides for the presence of C_{70} in the product prepared by the process of claim 141.

As we have found above, the product of Huffman et al.'s process before work-up and purification is graphitic soot including "a few" percent of C_{60} and even less C_{70}. Because none of the references on which we have relied discloses that fullerenes found in the earth's crust are found naturally in a small fraction of graphitic soot but rather are found in certain ores, it follows that none of the articles describe a product comprising C_{60} recovered from graphitic soot containing small amounts of C_{60} and even less C_{70}. Accordingly, the articles of record on which we relied do not present a bar under 35 U.S.C. § 101 to product-by-process claims 53, 119 or 141.

"COLOR"

It is stated by Huffman et al. that claim 86 distinguishes from naturally occurring fullerenes by reciting "a color for the product." However, only Huffman et al.'s claim 76 recites a color for the product. We shall presume that Huffman et al. intended their argument to apply to claim 76.

The only evidence in this record which establishes any color for the fullerenes claimed by Huffman et al. is the videotape (Huffman et al. Exhibit 3). The videotape shows the crystallization of fullerenes from a colored benzene solution with the formation of reddish brown crystals. The formation of the reddish brown crystals as the solvent evaporates is viewed through a microscope. Thus, it is the microscopic crystals dissolved in the benzene which imparted color to the benzene solution. Thus, Huffman et al.'s fullerenes, an allotrope of carbon, possess a reddish brown color.

We have not overlooked that the junior parties have alleged that claim 76 does not distinguish from certain diamond-containing ores which the junior parties allege are known to be earth-colored. That is, the junior parties assert that certain diamond-containing ores would be reddish brown and, thus, claim 76 reads on such naturally occurring diamond-containing ores. However, conspicuous by its absence in the record is any evidence which supports the junior parties' mere allegations. Accordingly, we reject the junior parties' representations as not founded on objective evidence.

Moreover, the articles on which we relied are silent as to what color, if any, the naturally occurring C_{60} might have.

Accordingly, from all the above, except for claims 82 and 87, we find all the Huffman et al. claims, which are claims designated as corresponding to Count 1, are not considered to be unpatentable under 35 U.S.C. § 101 because they do not "read on" the fullerenes shown to be found naturally in the earth's crust in ancient deposits because of the various claim limitations discussed above. Thus, Claims 45 through 81, 83 through 86 and 88 through 180[8], are not unpatentable under 35 U.S.C. § 101.

Huffman et al. have not argued in their brief that either claim 82 or 87 distinguish from the fullerenes described as found naturally in the earth's crust as described in the various articles of record. Neither claim 82 nor claim 87 include any of the above-discussed limitations which we found distinguished from the naturally occurring fullerenes. Accordingly, we find claims 82 and 87, corresponding to Count 1, to be unpatentable under 35 U.S.C. § 101.

PRIORITY

In Paper Number 38, we placed the junior parties under an order to show cause pursuant to 37 C.F.R. § 1.640(d)(3) as the junior parties' preliminary statements failed to overcome the effective filing date of the senior party. In response to the order to show

[8] Claim 134 is recited to depend from claim 11. There is no claim 11 pending in the Huffman et al. application.

cause, the junior party requested this final hearing (Paper Number 40).

The junior parties' only arguments on the issue of priority are the arguments raised by them below in various papers. That is, the junior parties allege there should be no priority contest because: there is no interference-in-fact; we lack jurisdiction; and this interference was improperly declared to include claims found to be unpatentable to the senior party by the examiner.

The junior parties argue that this interference should never have declared because the junior parties believe there is no interference-in-fact. We have exhaustively addressed that issue in this proceeding, including our finding above that an interference-in-fact exists between the claims of Ziolo's U.S. Patent Number 5,188,918, the claims of Mort et al.'s U.S. Patent Number 5,114,477 and the claims of Huffman et al.'s U.S. patent application Serial Number 07/580,246. The junior parties also allege that because there is no interference-in-fact, we lack any jurisdiction to initiate or continue these proceedings. This issue has also been exhaustively addressed in this proceeding in the decision on petition (Paper Number 12) and by this Board in this decision. The junior parties also allege that, to the extent this interference was declared to include claims of Huffman et al. indicated by the examiner as not allowable, it is improper. This issue, too, has been exhaustively addressed in this proceeding and above by us in our decision.

None of the junior parties' arguments are found to be persuasive on these issues. Accordingly, this proceeding will not include a priority phase because the junior party has failed to allege a date in their preliminary statements which overcomes the effective filing date of the senior party. However, the senior party raises a priority issue as an argument for patentability of their claims under 35 U.S.C. § 101 based on the allegation that their preliminary statement alleges a conception and reduction to practice of the subject matter of Count 1 in September 1983, which is before the date of Smalley et al.'s Nature publication in 1985.

As we understand Huffman et al.'s argument, because they allegedly conceived and reduced to practice their invention before the date of the Nature article published by Smalley et al., Smalley et al. cannot be considered to have "discovered" fullerenes.

However, a preliminary statement is merely a pleading which sets forth the metes and bounds of a party's priority case, which, if proved, serves as the basis for their argument that they are entitled to an award of priority. In this instance, because there is no priority contest between the parties, the mere allegations in the preliminary statement have never been proved and are nothing more than allegations. More significantly, even if proved, because this proceeding does not include Smalley et al. as a party, Huffman et al.'s allegations, even if proved, would not be determinative of the question of who, as between Smalley et al, and Huffman et al., invented or discovered fullerenes.

As we have decided the priority issue contrary to the junior parties and because the junior parties have not asserted any other persuasive reasons why we should not, on this record, declare Huffman et al. to be the first inventors of the subject matter of Count 1, we find Huffman et al. to be the first inventors of the subject matter of Count 1. Judgment in favor of the senior party and against the junior parties will be rendered forthwith hereinafter.

OTHER ISSUES

PATENTABILITY OF THE JUNIOR PARTIES' CLAIMS

The junior party has spent a significant portion of their briefs arguing that their patent claims are presumptively patentable and that we should not overturn that presumption (JB 35 through 44). However, the patentability of the junior parties' claims has neither been raised by us nor has the senior party moved for judgment against the junior parties on the grounds that any of the junior parties' claims designated as corresponding to Count 1 are unpatentable. Indeed, the patentability of the junior parties' claims is not in issue in this proceeding.

The only mention of the patentability of the junior parties' claims in this proceeding was with respect to our analysis as required under 37 C.F.R. § 1.601(n) to determine if an interference-in-fact existed between the parties to this interference and to determine if any of the junior parties' claims designated as corresponding to Count 1 should be designated as not corresponding to Count 1. In performing that analysis we made certain assumptions

with respect to the parties' claims which were required by 37 C.F.R. § 1.601(n). Those assumptions were just that. They were not findings by us with respect to the patentability of the junior parties' claims.

To the extent the junior parties are attempting to establish that our analysis under 37 C.F.R. § 1.601(n) was in error because, our conclusion that inks and toners using fullerenes as pigments would have been obvious from the fullerenes themselves is contrary to the determination of the examiner during the prosecution of the Ziolo II, we simply remind the junior parties that we are not bound by the determination of the examiner below. Sze v. Bloch, 458 F.2d 137, 173 USPQ 498 (CCPA 1972) (board of interferences is not bound by the *ex parte* determination of the board on a "right to make" issue). Heymes v. Takaya 6 USPQ2d 1448, 1453, 1454 (Bd. Pat. App. & Int. 1988). Nor is there a presumption of validity under 35 U.S.C. 282 of an issued patent involved in an interference. See Perkins v. Kwon, 886 F.2d 325, 327, 12 USPQ2d 1308, 1310 (Fed. Cir. 1989); Lamont v. Berguer, 7 USPQ2d 1580, 1582 (BPAI 1988). Compare also In re Etter, 756 F.2d 852, 225 USPQ 1 (Fed. Cir. 1985) (no presumption of validity of an issued patent in reexamination proceeding); In re Sneed, 710 F.2d 1544, 218 USPQ 385 (Fed. Cir. 1983) (no presumption of validity of an issued patent in a reissue application).

Further, this *inter partes* proceeding is founded on an entirely different record than was considered by the examiner during

the prosecution of Ziolo II. In performing our analysis under 37 C.F.R. § 1.601(n) we relied on certain evidence in this proceeding as the basis for our conclusion that fullerenes would have been expected to be useful pigments in inks and toners because they are obtained from and are a component of carbon black (graphitic soot) which evidence was not part of the record in the prosecution of Ziolo II.

We have not overlooked the junior parties' entreaty that we consider that fullerenes are said to have properties similar to graphite and that the junior parties established on the record during the prosecution of Ziolo II that graphite was not a suitable pigment for use in toners. Nevertheless, the basis for our determination that an interference-in-fact existed between the parties was founded on the disclosure in the evidence on which we relied that toners were known to comprise pigments dispersed in resins and that useful pigments or colorants included elemental carbon in more or less pure form, including carbon blacks and lampblacks. Thus, the relevance of the showing with respect to graphite *vis-à-vis* our conclusion founded on the disclosure of carbon blacks as useful pigments is not apparent on this record.

HUFFMAN ET AL.'S "RELATED" APPLICATIONS

The junior parties urge on page 18 of their main brief that Huffman et al., in Paper Number 66, refused to inform this Board about the existence of any pending, related patent applications directed to the process of making fullerenes. The junior parties

suggest that the Huffman et al.'s refusal to disclose such information is tantamount to a violation of their duty of disclosure under 37 C.F.R. § 1.56 and that "Board sanctions should be mandatory for this matter."

In the first instance, we are only authorized to issue sanctions for failure by a party to comply with the rules or any order issued by us. See 37 C.F.R. 1.616(a). We never ordered the senior party to inform us of the existence of any pending application directed to the process of making fullerenes in macroscopic amounts. Since we never ordered Huffman et al. to notify us of the existence of such applications, they cannot have violated an order we never issued. Even assuming, *arguendo*, such applications exist, the mere existence of such applications does not establish the materiality of such applications to this proceeding. We also observe that 37 C.F.R. § 1.656(b)(2) does not require a party to identify related applications but only "any related appeal or interference which is pending before the Board, or which has been decided by the Board," as "related" is defined in the last sentence of rule.

Finally, in their brief, Huffman et al. have included a statement of other related appeals and interferences. Therein Huffman et al. state unequivocally that they know of no appeals or interferences related to this proceeding (see page 1 of their brief). The rule requires no more and we have no reason to doubt Huffman et al.s' representation.

Nevertheless, we acknowledge receipt by electronic facsimile on June 4, 1998, of a paper directed to the attention of one member of this merits panel (Paper Number 83). We are unable to find any indication in said paper that this communication was served on the junior parties. However, 37 C.F.R. § 1.646 (a) requires all papers filed in an interference proceeding to be served on any and all parties. Accordingly, a copy of Paper Number 83 is attached to this decision and shall serve as the service required by the rule.

HUFFMAN ET AL.'S EXHIBIT 3

The junior parties have asserted in their reply brief that we should not consider Exhibit 3 (the videotape) in our deliberations because the tape constitutes hearsay (see page 20, paragraph 24 of the reply brief). Nonetheless, beyond their characterization of the tape as hearsay, the junior parties have not explained the basis for their hearsay objection to the tape. More significantly, the junior parties' briefs are replete with references to and reliance on the videotape for a variety of purposes beyond those portions of the tape which the junior parties have characterized as "admissions against interest". Even more significantly, the junior parties did not file a proper motion to suppress the tape under 37 C.F.R. § 1.656(h). We have considered the videotape to the extent indicated in this opinion and shall not suppress same as hearsay.

STATUTORY DISCLAIMER OF CLAIM 21 OF U.S. PATENT 5,114,477

In Paper Number 71, the junior parties have filed a statutory disclaimer of claim 21 in the Mort et al. patent, U.S.

Patent Number 5,114,477. Pursuant to 37 C.F.R. § 1.662(c), the disclaimer deletes claim 21 "from being involved in the interference." Because the disclaimer does not disclaim all the claims of Mort et al.'s patent designated as corresponding to Count 1, the disclaimer is not treated as a request for adverse judgment against Mort et al. The disclaimer has no other effect on this proceeding.

THE PARTIES' "STATEMENT OF FACTS"

At pages 3 through 9 of their brief and at pages 7 through 9 of their main brief and pages 15 through 20 of their reply brief, the senior party and the junior parties, respectively, have set forth proposed findings of fact. Additionally, Huffman have attached to their brief an attachment entitled "FINDINGS OF FACT". We acknowledge receipt of the findings but decline to either accept or reject the findings.

HUFFMAN ET AL.'S MATERIALS FILED UNDER 37 C.F.R. § 1.682

Attached to their brief, Huffman et al. have included a paper captioned "SUBMISSION UNDER 37 C.F.R. §1.682". We have considered the submission to the extent indicated above. We repeat that, contrary to Huffman et al.'s representations that the articles referenced therein rebut our finding that Smalley et al. "discovered" fullerenes, we find the articles establish that Smalley et al. are, indeed, recognized as the first to discover fullerenes.

OUTSTANDING *EX PARTE* ISSUES

Based on the record before us, it is herein ORDERED that the outstanding rejections of Huffman et al.'s claims corresponding to Count 1 shall be addressed by Huffman et al. before the examiner in light of any relevant findings herein when Huffman et al.'s involved application is returned to the examining group after this proceeding is terminated.

JUDGMENT

In light of our *sua sponte* granting of the junior parties' motion under 37 C.F.R. § 1.633(c)(4) based on our conclusion that claims 1 through 6 of Ziolo's U.S. Patent Number 5,232,810 do not correspond to Count 1, on this record, Ronald F. Ziolo is entitled to his U.S Patent Number 5,232,810 containing claims 1 through 6.

Judgment as to the subject matter of Count 1 is awarded against Joseph Mort and Mary A. Machonkin, a junior party. Joseph Mort and Mary A. Machonkin, a junior party, are not entitled to their patent containing claims 1 through 20 corresponding to Count 1.

Judgment as to the subject matter of Count 1 is awarded against Ronald F. Ziolo, a junior party. Ronald F. Ziolo, a junior party, is not entitled to his patent containing claims 1 through 18 corresponding to Count 1.

Judgment as to the subject matter of Count 1 is awarded against Donald R. Huffman and Wolfgang Krätschmer, the senior party. Donald R. Huffman and Wolfgang Krätschmer, the senior party are not

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman, et al. Examiner: Hendrickson

Serial No.: 07/580,246 Art Unit: 1754

Filed: September, 10th 1990 Docket: 7913Z

For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231

DECLARATION OF Raouf O. Loutfy

I, Raouf Loutfy, hereby declare:

1. I reside at 6507 N. Ventana Canyon Drive, Tucson, Arizona, USA.

2. I earned a B.Sc. degree in 1964 in Applied Chemistry from Cairo University, a M. Sc. in 1966 in Solid State Sciences from the American University, a Ph.D in 1971 in Physical Chemistry from University of Western Ontario, and a Diploma in Business Administration in 1976 from McGill University.

3. Between 1977 and 1981 I was employed as a group leader at Argonne National Laboratory in the Chemical Engineering Division.

4. Between 1981 and 1985 I was employed as Research Advisor of ARCO Metals/ARCO Chemical developing advanced material technologies.

5. Between 1985 to present I have been employed as president of MER Corporation, and since 1990 I have been involved in the commercial scale-up of fullerenes, and in developing applications for fullerenes.

6. I have published many articles, two books, and contributed a chapter in Encyclopedia of Technology on the fullerene production, and on applications of fullerenes. I have been an invited speaker to many technical and investment conferences as an expert in the technology and commercialization of fullerenes. I have received the prestigious Tibbetts award in 2001 from the Small Business Administration (SBA) for the commercialization of fullerenes.

For the convenience of the patent and trademark office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

7. I am intimately familiar with the published literature concerning fullerenes and I am personally involved in the research and development of new methods of production and applications for fullerenes including C_{60}, C_{70} and nanotubes.

8. I am informed by Mark J. Cohen, Esq., the attorney handling the prosecution of the subject United States patent application that a question has arisen concerning the use

of the term "macroscopic amounts" as applied to the fullerene products, e.g. C_{60} and C_{70} that are produced by the methods invented by Drs. Huffman and Kratschmer as described in the underlying application.

9. As set forth above, I have been professionally involved in the field of fullerenes development and manufacture since Dr. Huffman and Kratschmer disclosed their novel process for producing macroscopic quantities, i.e., visible quantities of fullerenes, e.g., C_{60} and C_{70}, as disclosed in the subject patent application and in their publication in Nature (1990) identified elsewhere in this Declaration and I am familiar with the use of the term "macroscopic quantities" in this field and, in general, in the scientific and academic communities.

10. I have read and reviewed the subject patent application, including the pending claims. It is my understanding that the subject application discloses, among other things, a process of producing fullerenes including C_{60} and C_{70} in macroscopic amounts and that, inter alia, U.S. Serial No. 07/580,246 includes claims directed to macroscopic quantities of C_{60} and C_{70}.

11. Although the subject patent application of Dr. Kratschmer and Huffman does not expressly use the term "macroscopic amounts" to describe the amounts of fullerenes, e.g., C_{60} and C_{70} first isolated by them, in accordance with the teaching of the process described therein, the fullerenes, e.g., C_{60} and C_{70}, that were prepared in accordance with the process described herein, were produced in measurable amounts that were visible to

them, and it is my professional opinion that these amounts are inherently amounts definable by the term "macroscopic amounts".

12. Part of our research and development at MER involves the use of various arc processes, plasma processes, and high temperature process to produce fine metal, ceramic, and carbon powders. In the course of this research and development work, MER has since from about 1985 to the present maintained equipment and capabilities that could have produced soot. I am quite familiar with the principal of operations and the use of such equipment. At MER, I regularly produced soot under arc, plasma, and high temperature conditions for various applications. I am also familiar with the work of the Nobel Laureate Sir Harry Kroto et al. al. published in Nature volume 318, No. 6042, 14-20 November 1985. p162. In this publication they report the detection of remarkably stable cluster of 60 carbon "atom" using time-of-flight mass spectrometry in the vapor phase. However, they never isolated or recovered visible particle of C_{60} and C_{70}, and did not disclose a process that would teach or lead others to do so. It is noted they reported the following "If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high".

13. On or about September 18, 1990, MER received and executed confidentiality agreement from RCT regarding disclosure to MER of Huffman's et al. al. discoveries.

14. On or about September 20, 1990, Dr. Huffman of U of A and Mr. Jacobs of RCT visited MER Corporation to further discuss proactive strategy concerning an arrangement

to license from RCT under the Huffman et. al. invention to produce fullerenes at MER and to capitalize on the fullerene discovery of Dr. Huffman et al., and to discuss in details the production and the separation of fullerenes from the vaporized carbon utilizing the Huffman et al. discoveries.

15. On October 9, 1990, Dr. Withers, CEO of MER, and I visited Dr. Huffman's laboratory and observed his apparatus and witnessed the operation of his apparatus for vaporization of carbon, and production and collection of soot containing fullerenes. In many respects, Dr. Huffman's apparatus was very similar to much of the equipment at MER; however, MER had not used their equipment to produce fullerenes prior to the Huffman et. al. invention. The operating conditions for such equipment and the realization of the existence of fullerenes in the soot were the missing elements, not only from MER's viewpoint, but also from that of all other researchers prior to the Huffman et. al. invention. The equipment of MER and others will not produce inherently fullerene and even if produced it was not known that it could be recovered as it was later taught by Dr. Kratschmer and Huffman. All researchers in this field either produced soot under high vacuum conditions, without sufficient concentration of carbon vapor, at low pressure, or without sufficient cooling or combination of these conditions to produce recoverable fullerenes in the soot. These conditions resulted in product that does not contain fullerenes. Even though it appears simple to the uninformed, especially in hindsight, the process of Dr. Kratschmer and Huffman as described in the subject application, is a remarkable discovery, which produced a high density of vapor of carbon as described on page 4 of the subject application which resulted in the formation of

macroscopic amounts of fullerenes by their method. From 1985, when Dr. Smally et. al. at Rice University discovered the existence of C_{60} and C_{70} atoms by spectrographic analysis of a vapor (see paragraph 12 above), until Dr. Huffman et. al. published their discovery in 1990 no one else realized how to produce and recover macroscopic quantities of these fullerenes, despite the availability of equipment that could have been used for this purpose.

16. I directed experiments to produce fullerene soot at MER using equipment at MER, and we also built additional low vacuum equipment based on the Kratschmer and Huffman method described in the subject application and produced macroscopic quantities of soot and fullerene. We separated the fullerene according to their teaching. From a similar apparatus as that described in the subject application, but operated for sufficient time, we were able to offer for sale to the research community fullerenes including pure (90%+) C_{60} and C_{70} by November 1990.

We have since developed computer control, fully automated reactor equipment using Kratschmer and Huffman's teaching in the subject application and we optimized the process to maximize the yield of fullerenes.

17. I repeated exactly the Huffman et. al. process according to the teaching described in the subject application including example 1 using ¼ inch in diameter graphite rod, at 100 torr Helium, using 100 ampere dc current. This graphite vaporized, and the vapor was condensed on a water cooled surface. The vaporization was performed for 50 minutes using about 17 cm length of the graphite rod and produced 12 gram of soot. The

fullerenes were recovered using tolerene and the amount of fullerene was determined. The yield of fullerene was about 8 to 10%. Accordingly, the total recoverable fullerenes was over 1.2 grams with over 900 mg of C_{60} and over 200 mg of C_{70} and the remaining other fullerenes.

According to the teaching in the subject application where they vaporized a ¼" graphite rod with 1 cm length, the inventor must have produced at least about 600 mg of soot that contains admixture of at least 63 mg of fullerenes that contain at least about 50 mg of C_{60} and at least about 10 mg of C_{70}. A 600-mg quantity of soot certainly can be seen by the naked eye, as also indicated by the inventor that "heavy block coating on collecting substrates and/or on the walls of the chamber which can be easily scraped off for the recovery step." Also, the 60 mg of fullerene certainly can be seen by the naked eye and it is measurable. Furthermore, the 45 and 10 mg of C_{60} and C_{70} respectively are also measurable, in today modern laboratory facility amount as low as 0.1 mg can be measured, and can be seen by the naked eye.

The same conclusion can be reached by simply calculating the mass of the rod vaporized in Kratschmer et al. subject application, including example 1, which is easily determined from the diameter of the graphite rod they used (1/4"), the length (1 cm), and typical density of the type of graphite used for graphite vaporization (2.0 g/cc). This calculation estimates that about 633 mg of soot containing fullerenes was produced by Kratschmer et al., which is certainly macroscopic and in agreement with the above-presented experimental data.

Moreover, if a longer graphite rod were used, the amount of C_{60}, C_{70} and other fullerenes produced would even be greater, as shown herein above.

18. It is in my opinion that the inventors of this subject application were the first to isolate and recover a measurable or macroscopic amount of fullurenes, and to teach others to do so. Their description in the application is clearly understood by ordinary skilled artisans, and when repeated by us allowed us to produce visible, measurable commercial quantities of fullerene product, commonly described as "macroscopic quantities".

19. It is also in my opinion that the inventors produced "macroscopic amounts" as used in the claims as clearly understood by the ordinary skilled artisan, and supported by the above. The term is commonly used to connote that amount which can be seen easily with the naked eye. This opinion is corroborated by the usage of this term by others in the fullerene field to describe the fullerene product produced by the process invented by Drs. Kratschmer and Huffman, for example, see the statement appearing at Column 1, lines 58-61 in U.S. Patent No. 6,077,401 issued June 20, 2000, on an application filed August 15, 1994, which is as follows:

> "All of these applications have been discovered since the first macroscopic amounts of the most common fullerene, C_{60}, were isolated in 1990 [Kratschmer, et al., Nature 347, 354 (1990)]."

The cited quote from the Fields et. al. patent also corroborates the common understanding of those familiar with the fullerene art that they were the first persons to produce fullerenes in macroscopic quantities and to show others how to do so.

For the convenience of the patent and trademark office, I have attached hereto as Exhibit 2 the cited patent.

I further declare that all statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. I acknowledge that willful false statement and the like are punishable by fine or imprisonment or both (18 U.S.C. §1001) and may jeopardize the validity of the application or any patent issuing thereon.

July 16, 2002
Date

Raouf O. Loutfy, Ph.D

Signed in Tucson, Arizona

Exhibit # 1

Curriculum Vitae of Dr. RAOUF O. LOUTFY

EDUCATION

Diploma	Business Administration, McGill University, 1976
Ph.D.	PhysicalChemistry/Electrohemistry, University of Western Ontario, 1971
M.Sc.	Solid State, American University, 1966
B.Sc.	Applied Chemistry, Cairo University, 1964

PROFESSIONAL EXPERIENCE

1999 – Present COO, FIC Corporation, New York, NY
Responsible for technical direction of this joint venture between MER, Mitsubishi Corporation, and RCT Corporation for the commercialization of Fullerene and Fullerene based materials.

1985 – Present President, MER Corporation, Tucson, Arizona
Responsible for developing advanced programs and technologies, managing research and development group, contract administration and financial responsibilities. Produced SiC whiskers, SiC Fibers, ceramic-ceramic composites, advanced lithium-ion battery technology, low cost bipolar plates for fuel cell. Lead a group to develop scale-up production of fullerenes, and its applications development.

1986 - 1988 President, Keramont Research Corp., Tucson. AZ
Responsible for building the infrastructure (equipment, personnel, and projects) for advanced materials research organization with emphasis on electronic ceramics, aluminum nitride substrates reinforcements (SiC_w, SiC_f and $TiB2_w$) and composites (ceramic-ceramic, and metal-ceramic. and intermetallic ceramic).

1981 - 1985 Research Advisor, ARCO Metals/ARCO Chemical Company, Tucson. AZ
Major responsibility in the development of advanced technology to produce primary light metals and advanced materials, and to provide company-wide support in area of expertise. These efforts result, amongst others, in a commercial plant for the production of high purity alumina.

1977–1981 Group Leader, Chemical Eng. Div., Argonne National Laboratory, IL
The major responsibility, as a group leader of the Electrolytic Technology Research Group, was to develop and implement a plan for the electrochemical technology for energy and resource saving. This was achieved by supporting and conducting research and development to improve industrial processes and identifying and developing new concepts of low energy alternative technologies. A second responsibility is the technical management of contracts in the electrolytic area and contracts for developing batteries for load-leveling applications.

1972-1977 Group Leader, Noranda Research Center, Pointe Claire, Quebec
In charge of developing advanced pyro metallurgical and electrometallurgical processes to improve plant operations and profitability. Those efforts led to the development of DSA anodes for metal winning, and a new oxidant for zinc purification process.

AWARDS

TITLE OF AWARD	DATE	PRESENTED BY	REASON FOR AWARD
Industrial R&D 100	1990	R&D Magazine	Development of SiC Fibers
Corporate Entrepreneur of the year	1990	AIN	Most Number of Contract Won in Arizona
Industrial R&D 100	1991	R&D Magazine	Development of SiC Whisker
Product of the Year	1991	AIN	Fullerenes Production
Industrial R&D 100	1996	R&D Magazine	PDS Powder
Tibbetts Award	1998	SBA	SBIR Commercialization
Tibbetts Award	2001	SBA	Commercialization of Fullerene

PUBLICATIONS AND PATENTS

- 24 U.S. patents (12 have been in the last 10 years)
- 12 patent disclosures
- 90 articles published
- A chapter on Hydrogenated Fullerene in the Encyclopedia of Technology
- 2 books, both on Fullerenes:

  D. Koruga, S. Hameroff, J. Withers, R.O. Loutfy, and M. Sundareshan "Fullerene, C60: History, Physics, Nanobiology, and Nanotechnology" Elsevier Science Publishing Co. New York, NY 1993.

  "Perspectives of Fullerene Nanotechnology", edited by Eiji Osawa, Kluwer Academic Publishers, February 2001.

The specific Chapters are:

1. R.O.Loutfy, A. Moravsky, A. Franco, and E.Veksler "Physical Hydrogen Storage on Nanotubes and Nanocarbon Materials"
2. R.O.Loutfy, S.Katagiri "Fullerene Materials for Lithium-ion Battery Applications"
3. R.O. Loutfy, S. Hossain, A. Moravsky and M. Saleh "Nanotubes as Anode Material for Lithium-ion Batteries"
4. Raouf O. Loutfy and Eugene M. Wexler "ABLATIVE AND FLAME-RETARDANT PROPERTIES OF FULLERENES"
5. R.O. LOUTFYJ. C. WITHERS, AND M. ABDELKADER "Development of Carbon Nanotube - Polymer Composites"
6. Raouf O. Loutfy, J.C.Withers and Stevan T. Dimitrijevic "USE OF FULLERENES AND CARBON NANOTUBES FOR FABRICATION OF EFFICIENT ELECTRON FIELD EMITTERS"
7. Raouf O. Loutfy, Eugene Weksler, and Weijiong Li "UNIQUE FULLERENE-BASED HIGHLY MICROPOROUS CARBONS FOR GAS STORAGE"
8. Raouf O. Loutfy, Timothy P. Lowe, Alexander P. Moravsky, and S. Katagiri "Commercial Production of Fullerenes and Carbon Nanotubes"
9. Raouf O. Loutfy, Eugene Weksler "GAS PHASE HYDROGENATION OF FULLERENES"

10. Raouf O. Loutfy, Eugene Weksler "HYDROGENATION OF ALKALI METAL – DOPED FULLERENES"
11. R.O.Loutfy, and M.Hecht "Aligned Carbon-Nanotubes for Sensor Applications"
12. Raouf O. Loutfy, Eugene Weksler "ADVANCED THERMAL PROTECTION COATING USING FULLERENES"

Other Fullerenes Publications:

S. Seraphin, J.C. Withers, R.O.Loutfy, et al, "TEM Studies of Nanotubes and Graphite Particles", Symposium of the Arizona Fullerene Consortium, November 6, 1992.

S. Seraphin, J.C. Withers, et al, "TEM Study of Carbon Nanotubes Produced by Various Processing Conditions," to be presented a John M. Crowley Symposium, Arizona State University, January 5-8, 1993.

S. Seraphin, J.Jiao, D. Zhou, J.C. Withers, R.O. Loutfy, "Effect of Processing Conditions on the Morphology and Yield of Carbon Nanotubes," *Carbon*, Vol 31, No 5, 685 (1993).

S. Seraphin, J. Jiao, D. Zhou, J.C. Withers, R.O. Loutfy, "Yttrium Carbide in Nanotubes," *Nature*, Vol. 362, April 8, 503 (1993).

J.C. Withers, R.O. Loutfy, K.Y. Donaldson, D.P. Hasselman, "Thermal Diffusivity/Conductivity of Compacts of C_{60} Buckminsterfullerene and a C_{60}/C_{70} Mixture, "*J.Am. Cerm. Soc.*, Vol 76, No 3, 754 (1993).

D. Koruga, J.S. Kustic, M. Trifunovic, S. Jankovic, S. Hameroff, J.C. Withers, R.O. Loutfy, "Imaging Fullerene C_{60} with Atomic Resolution Using a Scanning Tunneling Microscopy", *J. of Full. Science & Technology*, Vol 1, 93 (1993).

R.O. Loutfy, J.C. Withers, "Fullerene & Electrochemical Hydrogen Storage" abstract 2145, Electrochem. Soc. Mtg, Hawaii, (1993).

J.C. Withers, R.O. Loutfy, "Production Process for Fullerenes, Review" Abstract #2127 Electrochem. Soc. Meeting, Hawaii (1993).

T. Yadav, S. Seraphin, D. Zhou, J.C. Withers, R.O. Loutfy, "Catalytic Growth of Buckyonions," in preparation

S. Supapan, D. Zhou, J.Jiao, M. Minke, S. Wang, T. Yadav, J.C. Withers, R.O. Loutfy, "The Effect of Pt, Pd and Ni on the Synthesis of Carbon Clusters," in preparation

J.C. Withers, C. Pan, R.O. Loutfy, "Fullerene Price: How Low Will They Be?" Electrochemical Society Mtg., San Francisco, Abstract 1216, (1994)

Contracts

DOE contract #DE-FG02-92ER81272, "The Development of a Process to Synthesis Tubular Fullerenes", Phase II, July 92

DOE contract #DE-FG02-91ER81095, "Novel C_{60} Electrodes for Advanced Electrochemical Sensors", Phase I, Sept 91.

ARMY contract #DAAH04-93-C-0004, "Novel Materials for Hydrogen Supplies and Storage for Fuel Cells, Phase I, Jan 93.

ARMY contract #DASG60-93-C-0003, "Use of High Energy Lasers for Materials Synthesis", Phase I, Nov 92.

NASA contract #NAS5-32430 Goddard, "A Novel Negative Hydride Electrode for Ni-Metal Hydride Batteries", Phase I, Dec 92.

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman et al. Examiner: P. DiMauro

Serial No.: 08/236,933 Art Unit: 1103

Filed: May 2, 1994 Docket: 7913zazy

For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231

SUPPLEMENTAL DECLARATION OF HAROLD W. KROTO UNDER 37 C.F.R. §1.132

I, HAROLD W. KROTO, PH.D., declare and say as follows:

1. I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom (one of only twenty such appointments in the United Kingdom). In addition, I have been awarded over one dozen honorary degrees from various universities. In 1996, I, along with Robert Curl and Richard Smalley, received the Nobel Prize in Chemistry for our discovery of fullerenes. Earlier that year, I was also awarded Knighthood for my contributions to chemistry. For the convenience of the United States Patent and Trademark Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2. I am intimately familiar with the literature concerning and was personally involved in the search for C_{60} and other fullerenes. I have written several articles on the

subject, as evidenced by the publications listed in Exhibit 1, including the first definitive and only complete review on the subject in Kroto, et al., in Chemical Review 1991, 91, 1213 - 1235. I therefore believe that it is fair to say that I am among the recognized experts on the subject of fullerenes.

3. This Declaration supplements and is not intended to replace the previous Declarations which were executed on July 27, 1995 and June 9, 1995, the contents of which are incorporated herein by reference.

4. I have been requested by applicants' attorney to read and review the above-identified application, i.e., USSN 08/236,933 and the pending claims therein. In addition, I have been requested by applicants' attorney to comment on my understanding of the terms "macroscopic amounts" as applied to fullerenes, including C_{60}, in the claims and to comment on whether, in my opinion, the underlying specification clearly describes a process for making fullerenes, including C_{60}, in macroscopic amounts without an undue amount of experimentation.

5. As requested, I have read and reviewed the above-identified application, including the pending claims in the above-identified application. It is my understanding that the claims in the above identified application are directed, among other things, to a process of producing C_{60} in macroscopic amounts.

6. I have been advised that there is a companion application, USSN 486,669, on file in the United States Patent

and Trademark Office. I have been advised that, except for the claims, the disclosure in the '669 application is identical to that of the above-identified application. I have also reviewed the pending claims related thereto. It is my understanding that these claims are directed, among other things, to a process for making fullerenes in macroscopic amounts.

7. I have also been advised of the existence of two more applications, namely USSN 580,246 and USSN 471,890. It is my understanding that the former application is directed to, among other things, C_{60} in macroscopic amounts, while the latter is directed to, among other things, fullerenes in macroscopic amounts. It is also my understanding that, except for the claims, the respective specifications are not only identical, but also are identical to the specification of the above-identified application.

8. It is my opinion that the above-identified specification describes the preparation of fullerenes, including, for example, C_{60}, in macroscopic amounts. This is based upon my understanding of the application and my repetition of the procedure described in the underlying application for producing fullerenes, including C_{60}, and isolation thereof in macroscopic amounts.

9. It is my opinion that the term "macroscopic amounts" as used in the claims is clearly understood by the ordinary skilled artisan. It is my understanding that the term is being used in its plain and ordinary meaning to connote that

the process described in the underlying specification produces fullerenes, including, for example, C_{60}, in amounts which can be seen easily with the naked eye. This is consistent with the definitions of "macroscopic", as defined in the McGraw Hill Dictionary of Scientific and Technical Terms, 4th ed., p.1125, 1989, where it is defined as "large enough to be observed by the naked eye," and in Hackh's Chemical Dictionary, 4th ed., wherein it defines macroscopic as describing "objects visible to the naked eye."

10. "Fullerenes", in my opinion, is a term of art that is also widely understood by the scientific community; it was adopted to conveniently describe the family of caged carbon molecules represented by C_{60}. See, e.g., the section entitled "Fullerene" in the Concise Encyclopedia of Science and Technology, 3rd ed., Sybil P. Parker, ed., McGraw Hill, NY, NY, p. 819 (1994), attached hereto as Exhibit 2. This section, which was written by me, describes fullerenes as an even number of carbon atoms arranged in a closed hollow cage, and specifically exemplifies fullerene-60, or C_{60}, as a species of fullerenes. However, there are other species of fullerenes, and many of those can and have been prepared by the process described in the above-identified specification.

11. The above-identified application describes in great detail the process for producing fullerenes, including C_{60}. As an example thereof, attention is directed to Example 1 on Page 16 of the above-identified application which describes

a process for making fullerenes, including C_{60}, by (1) vaporizing graphite rods in a conventional bell jar evaporator in the presence of an inert quenching gas, e.g., helium or argon, to produce carbon smoke; (2) collecting the smoke formed; (3) then extracting the fullerenes, including C_{60}, using benzene, or other inert solvent; (4) then, after evaporating the solvent, subliming the impure product; and (5) then collecting the sublimed product.

12. The specification on Pages 3-8 describes a more general process for preparing fullerenes, including C_{60}, and describes other means for extracting fullerenes, including C_{60}, from the smoky carbon product, including sublimation and the use of other non-polar solvents to extract the fullerenes, including C_{60}, from the smoky carbon product.

13. It is my opinion that a person of ordinary skill in the art in 1990 reading the specification would understand the specification to be directed to the class of carbon structures that have come to be commonly referred to as fullerenes. There is no question that the specification describes, among other things, C_{60} and C_{70}, which are designated as fullerene-60 and fullerene-70, respectively. These are species of fullerenes, and the skilled artisan would comprehend that the specification is directed to fullerenes. Moreover, spectral data, especially mass spectra data of the smoky carbon product produced from the vaporization of the elemental carbon in the inert quenching gas, in accordance with the procedure

described in the above-identified application, reveals that the smoky carbon product contains other species of fullerenes; although not in the abundance of fullerene-60 or fullerene-70 nevertheless, collectively in macroscopic amounts in the soot. Moreover, at the time of September 1990, various other hollow caged species containing solely carbon atoms, now known as fullerenes, had been postulated. So even if not specifically mentioned in the application, these other species of fullerenes were inherently present in the carbon soot produced by the process described in the underlying application -- a fact verified by experimentation. Consequently, it is my opinion that the ordinary skilled artisan in 1990 would understand that the above-identified specification is directed to, among other things, a process for making fullerenes, including C_{60}.

14. Moreover, it is my opinion that the ordinary skilled artisan in September 1990 reading the specification would understand that the teachings therein were applicable for preparing and isolating not only C_{60} and C_{70}, but also other fullerenes without an undue amount of experimentation. Thus, the above-identified application paves the road for preparing and isolating other fullerenes species without an undue amount of experimentation.

15. Moreover, the specification provides evidence in several instances that the inventors had produced the fullerene products, including C_{60}, in macroscopic amounts. For example, attention is directed to Example 1 which describes the product

thereof in powder form as brownish-red. Such language connotes, in my opinion, that the product thereof could be seen with the naked eye. Moreover, based upon repetition of the process described therein, as described hereinbelow, the process as described in the above-identified application, especially in Example 1, inherently produces fullerenes, e.g., C_{60}, in amounts that could be seen with the naked eye.

16. Moreover, these concepts discussed in Paragraphs 13-15 are clearly corroborated when the ordinary skilled artisan repeats the procedures described in the above-identified specification for preparing the fullerenes.

17. Utilizing the procedure exactly as described in the above-identified application, I have had fullerenes, including C_{60}, prepared in macroscopic amounts on numerous occasions since 1990 to the present. More specifically, by following the procedure described in the above-identified application and vaporizing graphite rods in an atmosphere of helium, forming the carbon soot therefrom, collecting the soot and dissolving the soot in benzene, in accordance with the procedure described in the above-identified application, I and my colleagues have prepared and identified various fullerenes, including, inter alia, C_{60}, C_{70}, C_{76}, C_{78}, ~~C_{82}~~, C_{84} and C_{86}.

18. Moreover, by following the procedure described in the above-identified application, and in accordance with the procedure outlined in Paragraph 17 herein, ~~I~~ We have isolated fullerenes in macroscopic amounts, as defined herein. For

example, utilizing the procedure outlined in Paragraph 17, I have found that the smoky carbon product contains 5 to 10% C_{60} and 1% C_{70}. We routinely produce the soot in 1-5 gram quantities and routinely extract 100-500 milligram amounts batchwise. Thus, one kilogram of sooty carbon product produces, on average, 100g of C_{60}, 10g of C_{70} and 1 gram of other fullerenes, such as those indicated hereinabove. The various fullerenes formed can and are isolated in accordance with the isolation and purification procedures described in the above-identified application, without an undue amount of experimentation. Furthermore, the various fullerenes are isolated as solids, which are easily visible to the naked eye. For example, in a typical experiment conducted according to the procedure described in the above-identified application, C_{60} is formed in about 100 mg quantities C_{70} in about 10 mg quantities and the remainder in about 1 mg quantities.

19. Thus, by following the procedure described in the above-identified application, I have found that the process described therein inherently produces several species of fullerenes, including C_{60}, in macroscopic amounts. In fact, by following the procedure of Kratschmer and Huffman, outlined in the above identified application, crystalline material of fullerenes, including C_{60}, is produced which can be seen with the naked eye.

20. Moreover, there is additional evidence to support the statements made in Paragraph 19.

21. Attention is directed to an article by Kratschmer, et al. in Nature, 347, No. 6391, pp. 354-358 (1990), attached hereto as Exhibit 3. It was the first publication that describes the preparation and isolation of macroscopic amounts of a compound, e.g., C_{60} and C_{70}, having the fullerene structure.

22. It is interesting to note there are over 3,390 publications referring to their Nature article. Only a handful of papers in some fifty years of science receive this number of citations. It is apparent that the Nature article has been cited an innumerable number of times because various scientists have followed the procedures described therein to successfully produce macroscopic quantities of fullerenes, including C_{60}. The fact that several thousand publications reference the Nature article for preparing fullerenes adds further support that the procedure described in the Nature article and thus the present specification provides sufficient information for the skilled artisan to generally make macroscopic amounts of fullerene, including C_{60}, without an undue amount of experimentation. Moreover, it is also attributable to the due recognition by the scientific community of Kratschmer's and Huffman's claim to have originated this method of production.

23. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of C_{60} and C_{70} by the methods described in the above-identified application is recognized by the knowledgeable

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scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as C_{60} could be achieved by these methods, as it was generally expected that infinitesimal amounts of fullerenes would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

24. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite remarkable. The Kratschmer and Huffman method described in the above-identified application is all the more remarkable for the fact that so simple a procedure so readily produces large amounts of fullerenes. This is readily appreciated if one considers the historical perspective. Even since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 5, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my expert knowledge, one group, Huffman and Kratschmer, was

the first to find and publish a methodology capable of producing and isolating fullerenes, such as C_{60}, in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

25. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical prediction about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest, as evidenced by the 3390 citations to the Nature article in Exhibit 3 for making fullerenes. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating several thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes by making it possible for experimental researchers worldwide to study their chemical and physical properties.

26. The scientific community has unanimously and unequivocally acknowledged and recognized that Kratschmer and Huffman have developed a process for preparing fullerenes, e.g., C_{60}, in macroscopic amounts, and in consequence thereon has presented them with several awards. Even the press release by the Royal Swedish Academy of Sciences regarding the Nobel Prize in Chemistry in 1996, attached hereto as Exhibit 6, recognizes the contribution of Huffman and Kratschmer by

acknowledging that they for the first time produced "isolable quantities of C_{60}". (See Page 2 of Exhibit 6). As stated in the press release:

> [t]hey obtained a mixture of C_{60} and C_{70} the structures of which could be determined...The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}...An entirely new branch of chemistry developed with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics...

27. Thus, in my opinion, there is no reasonable doubt that the above-identified application describes a process for preparing fullerenes, including C_{60}, in macroscopic amounts and the process described therein provides sufficient detail for an ordinary skilled artisan in 1990 to make the same without an undue amount of experimentation.

28. I have reviewed pages 2-4 of the Office Action issued in the above-identified application and in USSN 486,669. In the Office Action in the above-identified application, the Office Action equates tonnage quantities with the term "macroscopic". It is my opinion that such logic is unjustified, since the skilled artisan would not equate "macroscopic amounts" with tonnage quantity. As defined hereinabove, macroscopic amounts is that amount which can be seen by the naked eye. As explained hereinabove, by following the procedure described in the application, macroscopic amounts of fullerenes, including C_{60}, are obtained. In fact, gram quantities are routinely available by the Kratschmer and

Huffman method described in the above-identified application, which amounts are in macroscopic amounts in accordance with the standard use of that term. Moreover, it is my opinion that the embodiment in the above-identified application can be modified without an undue amount of experimentation to produce fullerenes, including C_{60}, in a continuous process.

29. In USSN 486,669, the Office Action alleges that the application does not describe nor provide sufficient information to permit one skilled in the art to easily produce caged carbon molecules consisting solely of carbon atoms which are soluble in non-polar organic solvents. I disagree absolutely and totally. In my opinion, the term "caged carbon molecules consisting solely of carbon atoms which are soluble in non-polar organic solvents" uniquely describes fullerenes, and as indicated hereinabove, it is my opinion that the application describes the preparation of macroscopic amounts of fullerenes.

30. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so make are punishable by fine or imprisonment or both under section 1001 of Title 18 of the United States Code and that such willful false statements

may jeopardize the validity of the application or any patent issued thereon.

16th November 1999
DATE

HAROLD W. KROTO, PH.D.

CURRICULUM VITAE I

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Born 7th Oct 1939 Wisbech, Cambridgeshire, England.

Education

1947-58 Bolton School, Bolton, Lancashire.

1958-61 BSc, Sheffield, 1st class honours degree (Chemistry)

1961-64 PhD, Sheffield, *Electronic Spectroscopy of Unstable Molecules*; Supervisor: R N Dixon

1964-65 PDF, NRC (Ottawa) with D A Ramsay

1965-66 PDF, NRC (Ottawa) with C C Costain

1966-67 Memb. Tech. Staff, Bell Laboratories, Murray Hill, NJ (with Y H Pao, and D P Santry)

University Career (University of Sussex 1967-)
1967-68 (Tutorial Fellow); 1968-78 (Lecturer); 1978-85 (Reader)
1985-91 (Professor); 1991- (Royal Society Research Professor)

Awards

1981-82 Tilden Lecturer (Royal Society of Chemistry)
1990 Elected Fellow of the Royal Society
1991- Royal Society Research Professorship
1992 International Prize for New Materials
(American Physical Society/IBM, with R F Curl and R E Smalley)
Italgas Prize for Innovation in Chemistry
Université Libre de Bruxelles (DHC)
University of Stockholm (PhDHC)
Longstaff Medal 1993 (Royal Society of Chemistry)
Academia Europaea (Member)
1993 University of Limburg(DHC)
1994 Hewlett Packard Europhysics Prize
(with D R Huffman, W Krätschmer and R E Smalley)
Moet Hennessy*Louis Vuitton *Science pour l'Art* Prize
1995 University of Sheffield (Hon Degree)
University of Kingston (Hon Degree)
1996 Knighthood, Nobel Prize for Chemistry (with R F Curl and R E Smalley)
1997 University of Sussex (Hon Degree)
University of Helsinki (DHC)

Extra-university administration

SRC Millimetre Wave Telescope Sub-Committee 1977-81
SERC Millimetre Wave Telescope Users'Committee 1981-85
SERC Physical Chemistry Subcommittee 1987-90
SERC Synchrotron Radiation Facility Committee 1987-90
SERC Chemistry Committee 1988-91
IAU Sub-group on Astrophysical Chemistry 1987-
MBI Advisory Board of the Max Born Institute (Berlin) 1993-

RESEARCH

Main research areas:

I Spectroscopy of Unstable Species and Reaction Intermediates
(Infrared, Photoelectron, Microwave and Mass Spectrometry)

II Cluster Science
(Carbon and Metal Clusters, Microparticles, Nanofibres)

III Fullerenes
(Chemistry, Physics and Materials Science)

IV Astrophysics
(Interstellar Molecules and Circumstellar Dust)

Research Highlights:

a) Synthesis in 1976 of the first phoaphaalkenes (compounds containing the free carbon phosphorus double bond) in particular $CH_2=PH$ (with N P C Simmons and J F Nixon, Sussex), Refs 1,7.

b) Synthesis in 1976 of the first analogues of HCP, the phosphaalkynes which contain the carbon phoshorus triple bond - in particular CH_3CP (with N P C Simmons and J F Nixon, Sussex), Refs 2,7.

c) The discovery (1976-8) of the cyanopolyynes, HC_nN ($n=5,7,9$), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, Refs 3,7.

d) The discovery of C_{60}: Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), Refs 8,13,15.

e) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), Ref 9

f) The prediction that C_{60} should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) Ref 10

g) The explanation of why C_{70} is the second stable fullerene (after C_{60}) and the discovery of the *Pentagon Isolation Rule* as a criterion for fullerene stability in general (Refs 11,13,15)

h) The prediction of the tetrahedral structure of C_{28} and the possible stability of "tetravalent" derivatives such as $C_{28}H_4$ Refs 11,15.

i) The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), Refs 12,13.

j) The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C_{60} from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs 14,15.

k) The chromatographic separation/purification of C_{60} and C_{70} and ^{13}C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs 14,15.

Meetings (director, organiser or co-orgnaisor)

Brioni International Conferences 1988, 1990, 1993, ...,
Royal Society Discussion Meeting 1992
Fullerene Symposium 1993 (Santa Barbara)
Cursos de Verano (El Escorial) *Fullerenos* 1994

Editorial Boards

Chemical Society Reviews 1986- (Chairman 1990-)
Zeitschrift fur Physik D (Atoms Molecules and Clusters) 1992-
Carbon (1992-)
J. Chem. Soc. Chem. Comm. (1993-)

Research Details

University of Sheffield

1961-64	PhD in Free radical spectroscopy by flash photolysis

National Research Council

1964-65	Free radical spectroscopy by flash photolysis
1965-66	Microwave Spectroscopy

Bell Telephone Laboratories

1966-67	Raman Spectroscopy of Liquids, Quantum Chemistry

University of Sussex

1967-72	Free radical spectroscopy/flash photolysis
1967-73	Liquid phase interactions/Raman Spectroscopy
1970-	Unstable species/Microwave Spectroscopy
1972-90	Unstable species/Photoelectron Spectroscopy
1976-	Interstellar Molecules/Radioastronomy
1983-90	Unstable species/Fourier Transform IR Spectroscopy
1985-	Cluster Studies/Carbon, Metals
1990-	Fullerene Chemistry, Carbon nanostructures

Temporary Appointments (Visiting Professorships etc)

1974	Visiting Associate Professor, UBC Vancouver (3 months)
1976	Visiting Scientist, NRC Ottawa (3 wks)
1978	Visiting Scientist, NRC Ottawa (3 wks)
1981	Visiting Professor, USC (3 months).
1983	British Council Visitor, Inst Rudjer Boskovic (Zagreb)
1987	CNRS (1 month) Univ Paris Sud (Orsay)
1988-	Visiting Professor UCLA (Astronomy)
1996	Senior Visiting Research Fellow (UC Santa Barbara)

Extramural Activities

Sport

Tennis and Squash for Sheffield University (1959-1964).
University Athletics Union Finalists - Tennis (1962 and 1963)
President of Athletics Council, Sheffield University (1963-64)

Television Film

Chairman of Board of *VEGA SCIENCE TRUST*
Executive producer of seven 1-hour Television Films of Royal Institution Discourses for Vega/BBCFocus

Graphic Art and Design

Art Editor *Arrows* Sheffield University Arts Magazine 1962-64

PUBLICATIONS

240 research papers; book "*Molecular Rotation Spectra*" (Wiley 1975 - reprinted with a new preface Dover 1992)

Key Publications

1) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospha-alkenes $CF_2=PH$, $CH_2=PCl$ and $CH_2=PH$', *J.C.S. Chem. Comm.*, 513-515 (1976).

2) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne, CH_3CP, by microwave spectroscopy', *Chem. Phys. Letts.*, 42, 460-461 (1976).

3) A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne, HC_5N', *J. Mol. Spectrosc.*, 62, 175-180 (1976).

4) L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', *Astrophys. J.*, 205, L173-175 (1976).

5) H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, 'The Detection of Cyanohexatriyne, HC_7CN, in Heiles' Cloud 2', *Astrophysics J.*, 219, L133-L137 (1978).

6) N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of HC_9N in Interstellar Space', *Astrophys. J.*, 223, L105-107 (1978).

7) H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; *Chem. Soc. Revs.*, 11, 435-491 (1982).

8) H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, 'C_{60}: Buckminsterfullerene', *Nature*, 318(No.6042), 162-163,(1985)

9) J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, H W Kroto, F K Tittel and R E Smalley 'Lanthanum Complexes of Spheroidal Carbon Shells', *J. Am. Chem. Soc.*, 107, 7779-7780 (1985).

10) Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley. 'Reactivity of large carbon clusters Spheroidal Carbon Shells and their possible relevance to the formation and morphology of soot', *J. Phys. Chem.*, 90, 525-528 (1986)

11) H W Kroto, 'The Stability of the Fullerenes C_n (n = 24, 28, 32, 50, 60 and 70)', *Nature* 329, 529-531 (1987)

12) H W Kroto and K McKay, 'The Formation of Quasi-icosahedral Spiral Shell Carbon Particles' *Nature*, 331, 328-331 (1988)

13) H W Kroto "Space, Stars, C_{60} and Soot", *Science*, 242, 1139-1145 (1988)

14) R Taylor, J P Hare, A K Abdul-Sada, and H W Kroto, "Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70}: The Third Form of Carbon." *J. Chem. Soc. Chem. Commun.*, 1423-1425 (1990)

15) H W Kroto "C_{60}: Buckminsterfullerene, the Celestial Sphere that Fell to Earth", *Angewandte Chemic* 31, 111-129 (1992)

Winner of *Sunday Times* Book Jacket Design Competition 1963
Editor, design and layout of *Chemistry at Sussex*
Cover design featured in *Modern Publicity 1979* (international annual of Graphic Design)
Publicity and logos for Chemical Society Meetings
Logo, letterheads for Science and Engineering at Sussex
Publicity, logo, letterheads, poster for BA Meeting 1983
New Scientist BA Advertisement
Logo and letterhead for Inorganic Biochemistry Discussion Group
Logo and letterhead 1990 for *Venture Research International*
(Formerly *BP Venture Research*)
New Cover design and layout for *Chemical Society Reviews*

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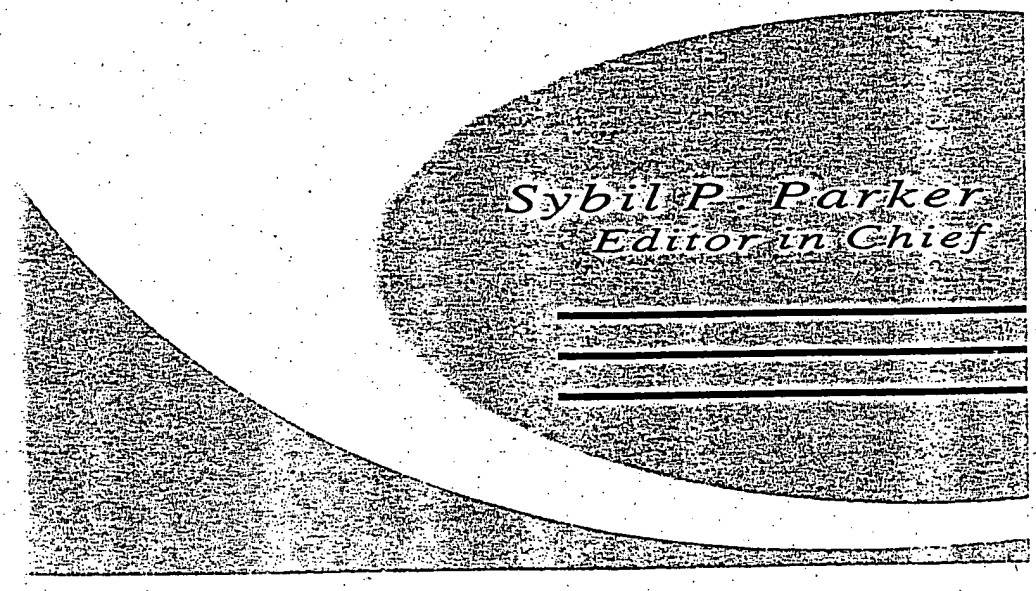

Sybil P. Parker
Editor in Chief

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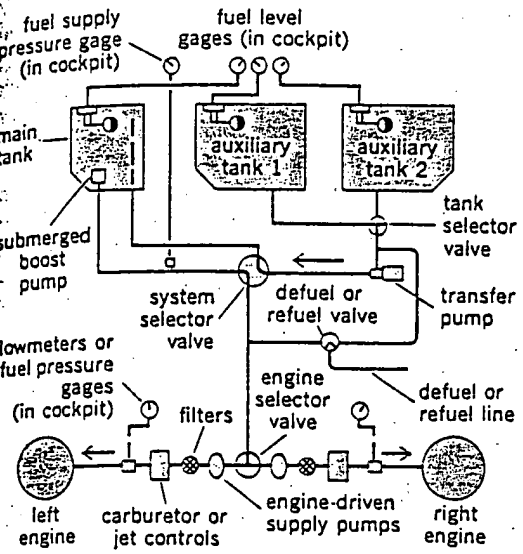


Diagram of a typical aircraft fuel system.

is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxiliary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly. [F.C.M./J.A.B.]

Fugacity A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity f_i of a constituent i of a thermodynamic system is defined by the following equation (where μ_i is the chemical

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

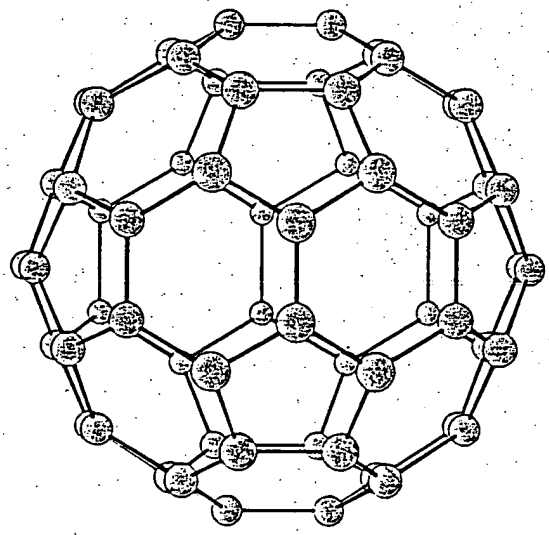
potential and μ_i° is a function of temperature only), in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value for μ_i°, which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1 atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. *See* ACTIVITY (THERMODYNAMICS); CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; GAS. [P.J.B.]

Fullerene A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. *See* CARBON.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene (C_{60} or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and n hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the sp^2 sigma-bonding skeleton, and the fourth p electron is one of 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of pi electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. *See* ELECTRON CONFIGURATION; GRAPHITE.

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammonated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom [for example, lanthanum (La), potassium (K), or calcium (Ca)] is trapped inside the cage.



Structure of C_{60} (buckminsterfullerene).

Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

Fullerene-60 was discovered as a direct result of physicochemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture. [H.W.K.]

Fuller's earth Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.

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A NEW FORM OF CARBON

UNDERSTANDING ANTARCTIC OZONE DEPLETION

The cellular defect behind cystic fibrosis

Solid C_{60}: a new form of carbon

W. Krätschmer*, Lowell D. Lamb†, K. Fostiropoulos* & Donald R. Huffman†

* Max-Planck-Institut für Kernphysik, 6900 Heidelberg, PO Box 103980, Germany
† Department of Physics, University of Arizona, Tucson, Arizona 85721, USA

A new form of pure, solid carbon has been synthesized consisting of a somewhat disordered hexagonal close packing of soccer-ball-shaped C_{60} molecules. Infrared spectra and X-ray diffraction studies of the molecular packing confirm that the molecules have the anticipated 'fullerene' structure. Mass spectroscopy shows that the C_{70} molecule is present at levels of a few per cent. The solid-state and molecular properties of C_{60} and its possible role in interstellar space can now be studied in detail.

FOLLOWING the observation that even-numbered clusters of carbon atoms in the range C_{30}–C_{100} are present in carbon vapour[1], conditions were found[2–4] for which the C_{60} molecule could be made dominant in the large-mass fraction of vapourized graphite. To explain the stability of the molecule, a model was proposed of an elegant structure in which the carbon atoms are arranged at the 60 vertices of a truncated icosahedron, typified by a soccer ball. The structure, dubbed buckminsterfullerene[2] because of its geodesic nature, has been the subject of several theoretical stability tests[5,6] and has been discussed widely in the literature. Calculations of many physical properties have been made, including electron energies[7–9], the optical spectrum[9], vibrational modes[10–15], and the electric and magnetic properties[16,17]. There has been speculation on the possible chemical and industrial uses of C_{60} (ref. 2), and on its importance in astrophysical environments[18–20]. Until now, it has not been possible to produce sufficient quantities of the material to permit measurement of the physical properties, to test the theoretical calculations, or to evaluate the possible applications.

Some of us have recently reported evidence[21,22] for the presence of the C_{60} molecule in soot condensed from evaporated graphite. The identification was based primarily on the observed isotope shifts of the infrared absorptions when ^{12}C was replaced by ^{13}C, and on comparison of the observed features with theoretical predictions. The measured infrared and ultraviolet absorption bands were superimposed on a rather large continuum background absorption from the graphitic carbon which comprised ≥95% of the sample. Here we report how to extract the carrier of the features from the soot, how to purify it, and evidence that the material obtained is in fact primarily C_{60}.

Method of production

The starting material for our process is pure graphitic carbon soot (referred to below as simply soot) with a few per cent by weight of C_{60} molecules, as described in refs 21, 22. It is produced by evaporating graphite electrodes in an atmosphere of ~100 torr of helium. The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene. The material giving rise to the spectral features attributed to C_{60} dissolves to produce a wine-red to brown liquid, depending on the concentration. The liquid is then separated from the soot and dried using gentle heat, leaving a residue of dark brown to black crystalline material. Other non-polar solvents, such as carbon disulphide and carbon tetrachloride, can also dissolve the material. An alternative concentration procedure is to heat the soot to 400 °C in a vacuum or in an inert atmosphere, thus subliming the C_{60} out of the soot (W. Schmidt, personal communication). The sublimed coatings are brown to grey, depending on the thickness. The refractive index in the near-infrared and visible is about two. To purify the material, we recommend removing the ubiquitous hydrocarbons before the concentration procedure is applied (for example, by washing the initial soot with ether). Thin films and powder samples of the new material can be handled without special precautions and seem to be stable in air for at least several weeks, although there does seem to be some deterioration with time for reasons that are as yet unclear. The material can be sublimed repeatedly without decomposition. Using the apparatus described, one person can produce of the order of 100 mg of the purified material in a day.

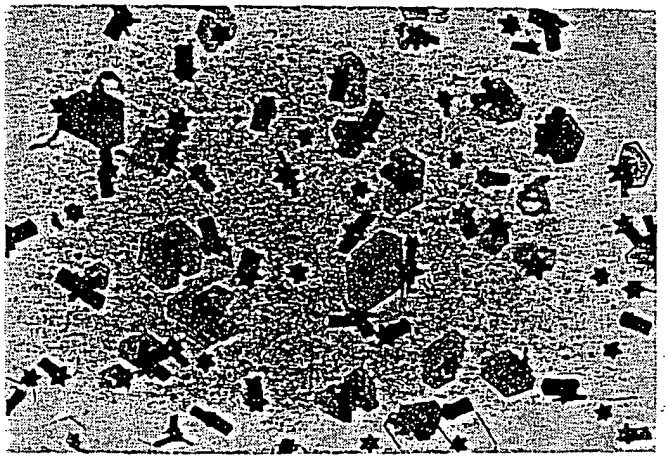

FIG. 1 Transmission micrograph of typical crystals of the C_{60} showing thin platelets, rods and stars of hexagonal symmetry.

Studies by optical microscopy of the material left after evaporating the benzene show a variety of what appear to be crystals—mainly rods, platelets and star-like flakes. Figure 1 shows a micrograph of such an assemblage. All crystals tend to exhibit six-fold symmetry. In transmitted light they appear red to brown in colour; in reflected light the larger crystals have a metallic appearance whereas the platelets show interference colours. The platelets can be rather thin and are thus ideally suited for electron-diffraction studies in an electron microscope (see the inset in Fig. 3).

Mass spectroscopy

The material has been analysed by mass spectrometry at several facilities. All mass spectra have a strong peak at mass 720 a.m.u., the mass of C_{60}. Significant differences in the spectra occur only at masses lower than 300 a.m.u. Most of these differences seem to originate from the different ionization techniques and in the different methods of desorbing molecules from the sample. Mass spectra recorded at low and high resolution are shown in Fig. 2. The spectra were obtained using a time-of-flight secondary-ion mass spectrometer[23] and a C_{60}-coated stainless-steel plate. In the mass range above 300 a.m.u., the spectrum is dominated by C_{60} ions and its fragments (even-numbered clusters of atomic carbon), and C_{70} ions. In this sample, the ratio of C_{70} to C_{60} is

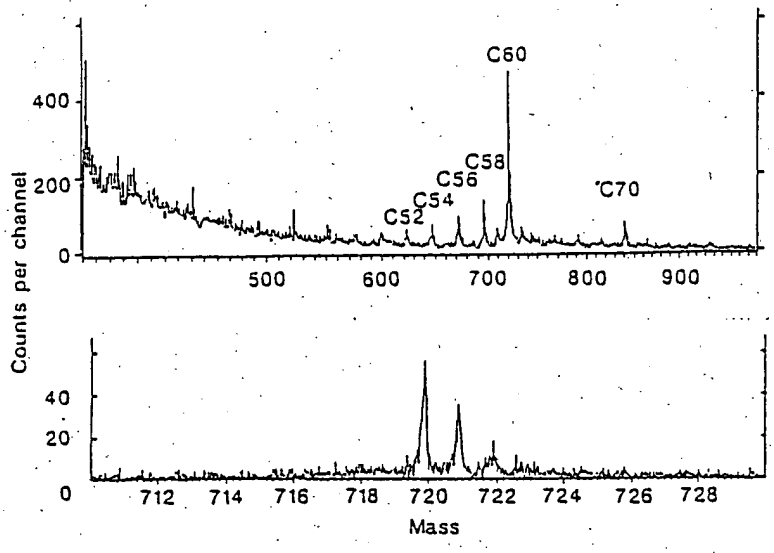

FIG. 2 Low-resolution (top) and high-resolution time-of-flight mass spectra of positive ions obtained from coatings of solid C_{60}. A 5-keV Ar^+ ion beam was used to sputter and ionize the sample. The isotope pattern (bottom) is approximately that expected for C_{60} molecules composed of ^{12}C and ^{13}C isotopes of natural abundance.

−0.1. The high-resolution mass spectrum shows approximately the expected isotope pattern for C_{60}. The increasing background in the low-resolution mass spectrum is not produced by the sample—such backgrounds also occur in blank measurements on uncoated stainless-steel substrates.

So far, the cleanest mass spectra have been obtained when the material was evaporated and ionized in the vapour phase by electrons. In such spectra the low-mass background is substantially reduced and the entire mass spectrum is dominated by C_{60} ions and its fragments. The ratio of C_{70} to C_{60} in these mass spectra is −0.02 and seems to be smaller than that shown in Fig. 2. Both ratios are of the order of those reported from laser-evaporation experiments[2,3]. We assume, as previously suggested[24], that the C_{70} molecule also has a closed-cage structure, either elongated[24] or nearly spherical[25]. Further details of the mass spectroscopy of the new material will be published elsewhere.

Structure

To determine if the C_{60} molecules form a regular lattice, we performed electron and X-ray diffraction studies on the individual crystals and on the powder. A typical X-ray diffraction pattern of the C_{60} powder is shown in Fig. 3. To aid in comparing the electron diffraction results with the X-ray results we have inset the electron diffraction pattern in Fig. 3. From the hexagonal array of diffraction spots indexed as shown in the figure, a d spacing of 8.7 Å was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The most obvious correspondence between the two types of diffraction is between the peak at 5.01 Å of the X-ray pattern and the (110) spot of the electron diffraction pattern, which gives a spacing of ~5.0 Å. Assuming that the C_{60} molecules are behaving approximately as spheres stacked in a hexagonal close-packed lattice with a c/a ratio of 1.633, d spacings can be calculated. The results are shown in Table 1. The values derived from this interpretation are $a = 10.02$ Å and $c = 16.36$ Å. The nearest-neighbour distance is thus 10.02 Å. For such a crystal structure the density is calculated to be 1.678 g cm^{-3}, which is consistent with the value of 1.65 ± 0.05 g cm^{-3} determined by suspending crystal samples in aqueous $GaCl_3$ solutions of known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions suggest that the order is less than perfect. Further, X-ray diffraction patterns from carefully grown crystals up to 500 μm in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micrometre-sized crystals). It therefore appears that these larger crystals do not exhibit long-range periodicity in all directions.

A likely explanation for these facts lies in the disordered stacking of the molecules in planes normal to the c axis. It is well known that the positions taken by spheres in the third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in a face-centred cubic structure being ABCABC... whereas that in a hexagonal close-

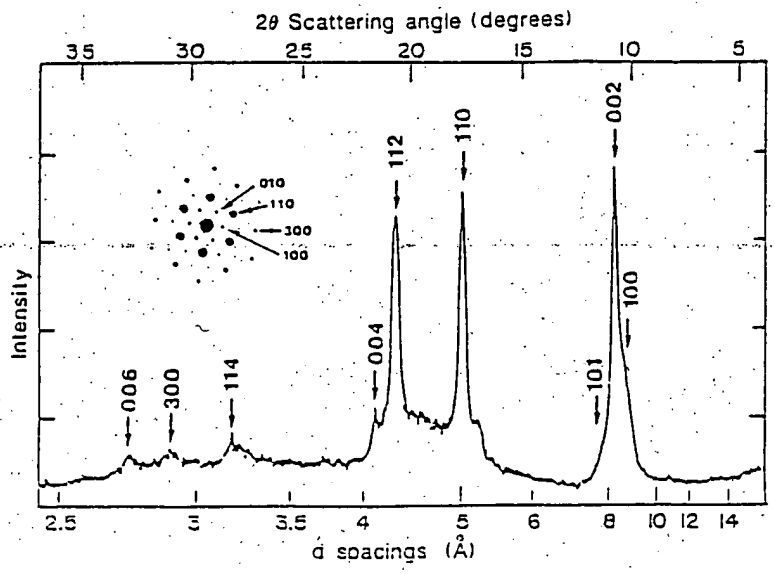

FIG. 3 X-ray diffraction pattern of a microcrystalline powder of C_{60}. Inset (upper left) is a single-crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern. The pattern is from a thin platelet such as those in Fig. 1 with the electron beam perpendicular to the flat face.

TABLE 1 X-ray diffraction results

Measured 2θ (deg)	Measured d spacing (Å)	Calculated d spacing (Å)	Assignment (hkl)
10.2 shoulder	8.7	8.68	(100)
10.81	8.18	8.18	(002)
		7.68	(101)
17.69	5.01	5.01	(110)
20.73	4.28	4.28	(112)
21.63	4.11	4.09	(004)
28.1	3.18	3.17	(114)
30.8	2.90	2.90	(300)
32.7	2.74	2.73	(006)

Assignments for a hexagonal lattice using $a = 10.02$ Å, $c = 16.36$ Å. $(1/d^2) = \frac{4}{3}[(h^2 + hk + k^2)/a^2] + l^2/c^2$.

packed structure is ABABAB ... If the stacking sequence varies, the X-ray lines owing to certain planes will be broadened by the disorder whereas other lines will remain sharp. Such disordered crystalline behaviour was observed long ago in the hexagonal close-packed structure of cobalt[26-28] where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened by the stacking disorder. Reflections from planes such as (002) remain sharp because these planes have identical spacings in the face-centred cubic and hexagonal close-packed structures. For the planes producing broadened diffraction peaks because of this kind of disorder, the following condition for the Miller indices (hkl) has been shown to apply[27,29]: $h - k = 3t \pm 1$ (where t is an integer) and $l \neq 0$. None of these broadened reflections are apparent in the X-ray pattern of Fig. 3. This may explain the weakness of the characteristically strong (101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated C_{70} molecule has yet to be determined.

In small crystals at least, the C_{60} molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, which is entirely consistent with the hypothesis that they are shaped like soccer balls. The excess between the nearest-neighbour distance (10.02 Å) and the diameter calculated for the carbon cage itself (7.1 Å) must represent the effective van der Waals diameter set by the repulsion of the π electron clouds extending outward from each carbon atom. Because the van der Waals diameter of carbon is usually considered to be 3.3–3.4 Å the packing seems a little tighter than one might expect for soccer-ball-shaped C_{60} molecules. The reason for this has not yet been determined.

In summary, our diffraction data imply that the substance isolated is at least partially crystalline. The inferred lattice constants, when interpreted in terms of close-packed icosahedral C_{60}, yield a density consistent with the measured value. Further evidence that the molecules are indeed buckminsterfullerene and that the solid primarily consists of these molecules comes from the spectroscopic results.

Spectroscopy

The absorption spectra of the graphitic soot[21,22] showed evidence for the presence of C_{60} in macroscopic quantities. Following the purification steps described above the material can be studied spectroscopically with the assurance that the spectra are dominated by C_{60}, with some possible effects from C_{70}. Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimation chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of C_{60} smoke (sub-micrometre microcrystalline particles of solid C_{60}) with the particle size depending to some extent on the pressure.

Figure 4 shows the transmission spectrum of an ~2-μm-thick C_{60} coating on a silicon substrate. The infrared bands are at the same positions as previously reported[21,22], with the four most

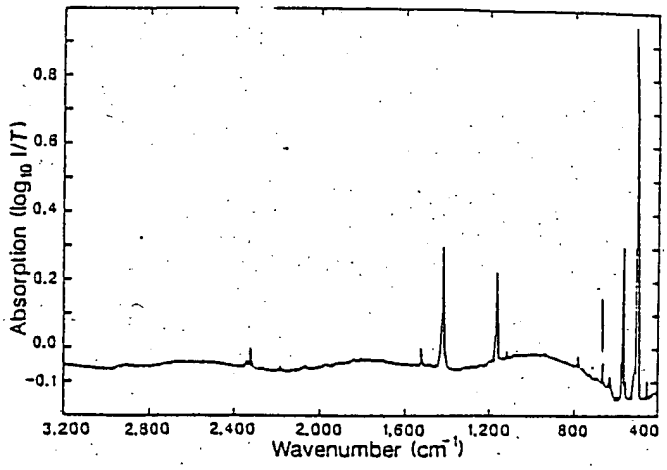

FIG. 4 Infrared absorption spectrum of a coating, ~2 μm thick, of solid C_{60} on a silicon substrate, referenced to a clean silicon substrate. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

intense lines at 1,429, 1,183, 577 and 528 cm^{-1}; here, however, there is no underlying continuum remaining from the soot. In many of our early attempts to obtain pure C_{60}, there was a strong band in the vicinity of 3.0 μm, which is characteristic of a CH-stretching mode. After much effort this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Fig. 4 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities. Vibrational modes to compare with the measured positions of the four strong bands have been calculated by several workers[10-15]. As noted previously, the presence of only four strong bands is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the C_{70} molecule or symmetry-breaking produced (for example) by isotopes other than ^{12}C in the C_{60} molecule or by mutual interaction of the C_{60} molecules in the solid. Weaker features at ~2,330 and 2,190 cm^{-1}, located in the vicinity of the free CO_2 and CO stretching modes, may imply some attachment of the CO_2 or CO to a small fraction of the total number of C_{60} molecules. Another notable feature is the peak at 675 cm^{-1}, which is weak in the thin-film substrates but almost as strong as the four main features in the crystals. We suspect that this vibrational mode may be of solid state rather than molecular origin.

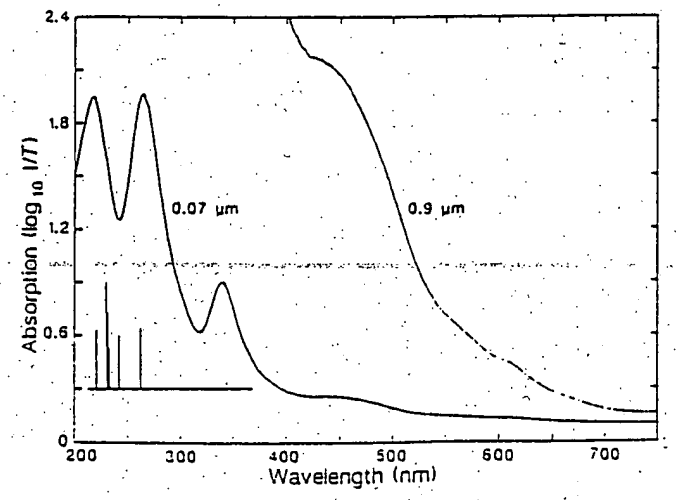

FIG. 5 Visible–ultraviolet absorption spectra of two thicknesses of solid C_{60} on quartz. The calculated[3] positions and relative oscillator strengths for allowed transitions of C_{60} are shown on the bottom.

Figure 5 shows an absorption spectrum taken on a uniform film coated on a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra[22]. Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a plateau between ~460 and 500 nm and a small peak near 625 nm. At the bottom of Fig. 5 we have shown positions and relative oscillator strengths taken from Larsson, Volosov and Rosén[9] calculated for the C_{60} molecule. They also reported a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between our measurements on solid films and the allowed transitions predicted for the molecule. The possibility exists, however, that one or more of the absorption features shown in Fig. 5 are due to C_{70}. We still do not observe a band at 386 nm in our films, as observed[30] using a laser depletion spectroscopy method and attributed to the C_{60} molecule. Quite similar spectra to that in Fig. 5 have been recorded for microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268 and 345 nm.

Possible interstellar dust

The original stimulus for the work[2] that led to the hypothesis of the soccer-ball-shaped C_{60} molecule, buckminsterfullerene, was an interest in certain unexplained features in the absorption and emission spectra of interstellar matter. These include an intense absorption band at 217 nm which has long been attributed to small particles of graphite[31], a group of unidentified interstellar absorption bands in the visible that have defied explanation for more than 70 years[31,32], and several strong emission bands attributed to polycyclic aromatic hydrocarbons[33,34]. Based on the visible and infrared absorption spectra of Figs 4 and 5, we do not see any obvious matches with the interstellar features. The ultraviolet band at 216–219 nm has a similar peak wavelength to an interstellar feature, although the other strong bands of the spectrum have no interstellar counterparts. As the influence of C_{70} absorptions on the spectrum is not yet known, a conclusive comparison with the 217-nm interstellar band is difficult. We note that the visible–ultraviolet spectrum presented here is characteristic of a solid, rather than of free molecules. In addition, these new results do not relate directly to absorption in the free C_{60}^{+} molecular ion, which has been envisaged[19] to explain the diffuse interstellar bands. Nevertheless, these data should now provide guidance for possible infrared detection of the C_{60} molecule, if it is indeed as ubiquitous in the cosmos as some have supposed.

Summary

To our method for producing macroscopic quantities of C_{60}, we have added a method for concentrating it in pure solid form. Analyses including mass spectroscopy, infrared spectroscopy, electron diffraction and X-ray diffraction leave little doubt that we have produced a solid material that apparently has not been reported previously. We call the solid fullerite as a simple extension of the shortened term fullerene, which has been applied to the large cage-shaped molecules typified by buckminsterfullerene (C_{60}). The various physical and chemical properties of C_{60} can now be measured and speculations concerning its potential uses can be tested. □

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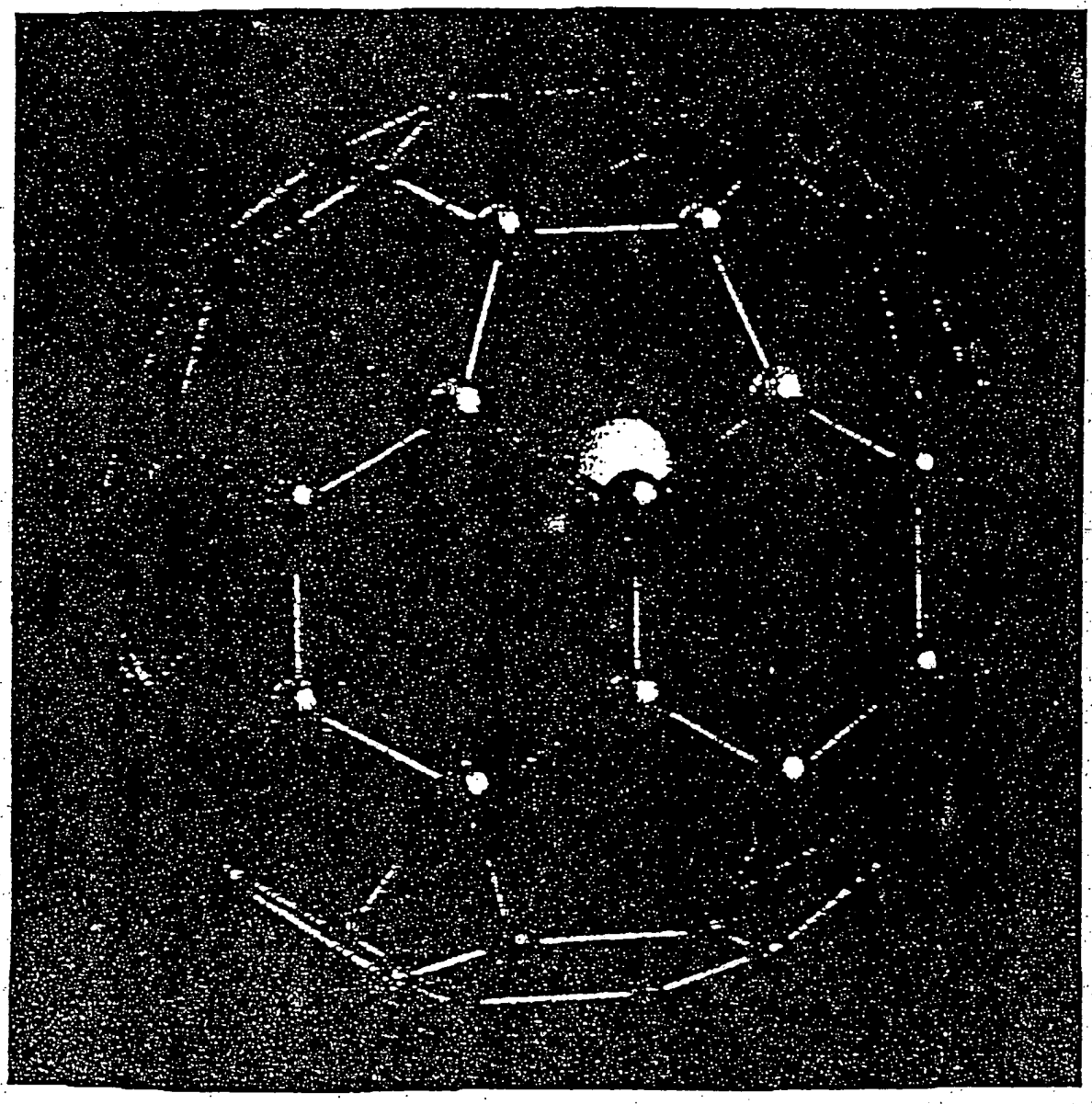
Remnants of a planet that failed to form.

Still no technological fix for oil spills.

What made higher life-forms possible?



Buckyball, the third form of pure carbon, cages an atom in its lattice.

Fullerenes

These cagelike molecules constitute the third form of pure carbon (the other two are diamond and graphite). C_{60}, the archetype, is the roundest molecule that can possibly exist

by Robert F. Curl and Richard E. Smalley

In May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent turned red.

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their collaborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tucson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fax, exchanging measurements of the material—its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this hollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had failed. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Texas, we celebrated, with champagne all around. For although we had to some extent been scooped, we had been vindicated as well. Five years earlier we had had our own Eureka! experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that C_{60} could be made in a uniquely stable form simply by laser-vaporizing graphite in a pulsed jet of helium. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Fuller, we named it buckminsterfullerene, or buckyball for short.

In addition to C_{60}, another molecule, C_{70}, appeared to be quite special in these early experiments. We soon found that the stability of C_{70} could be understood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and hexagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C_{60} has 20 hexagons, whereas the structure we proposed for C_{70} has 25, producing a shape reminiscent of a rugby ball.

In fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Fuller, it seemed fitting to term this entirely new class of molecules the "fullerenes."

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym "Daedalus" in the *New Scientist* in 1966, had conceived of a "hollow molecule" made of curled-up graphitic sheets. Others had predicted the stability of C_{60} from calculations and tried—unsuccessfully—to synthesize it. We, however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be perfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of them—billions and billions more.

Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collaborated for the past seven years in research on carbon and semiconductor clusters in supersonic beams. Curl is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quantum Institute.

HYPERFULLERENE STRUCTURE called a Russian egg is expected to form along with ordinary fullerenes in a laser-vaporized carbon plume. Shown here is the most symmetric form: a C_{60} at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in icosahedral alignment.

proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

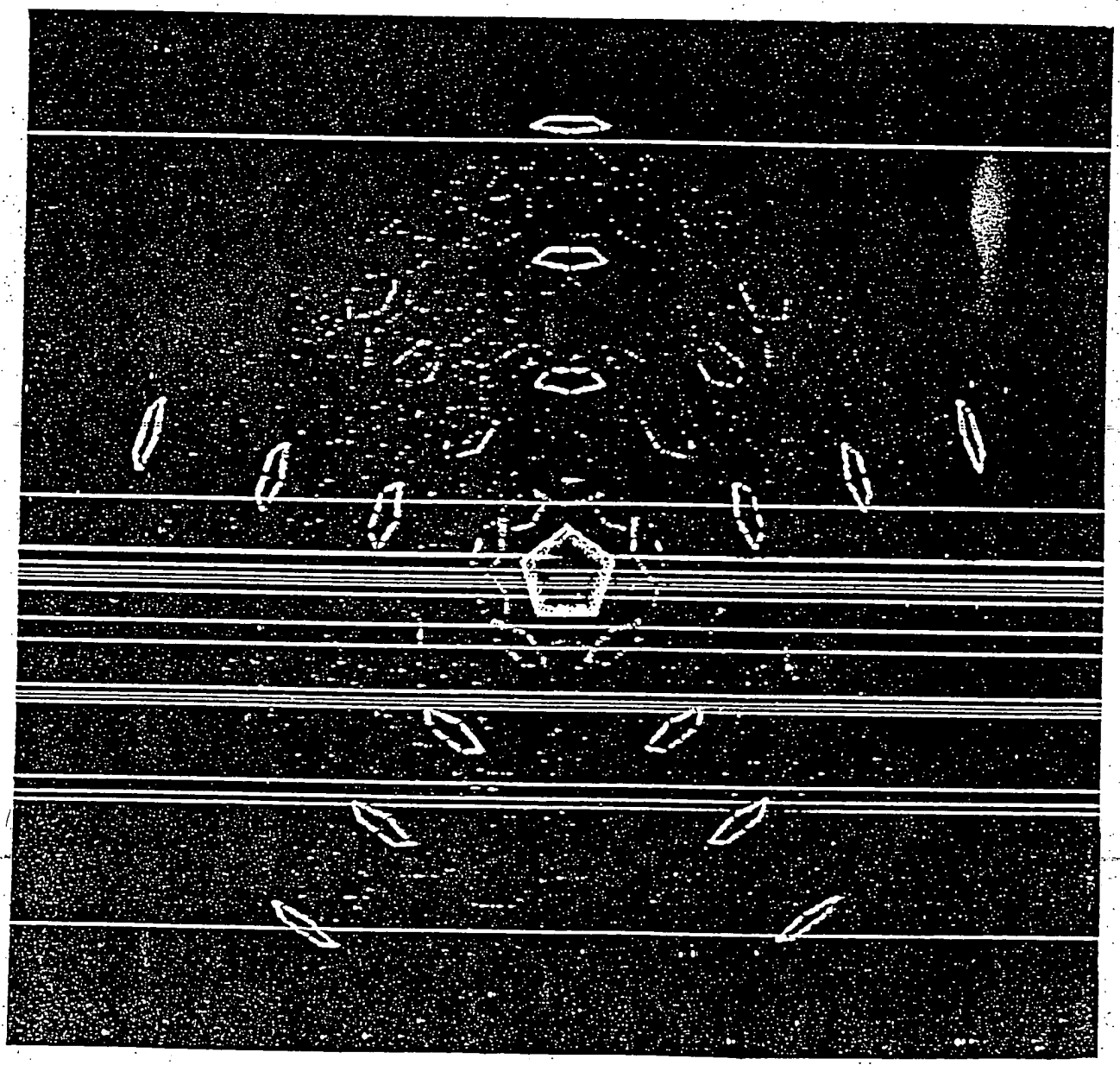
In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of C_{60}. We shirred the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

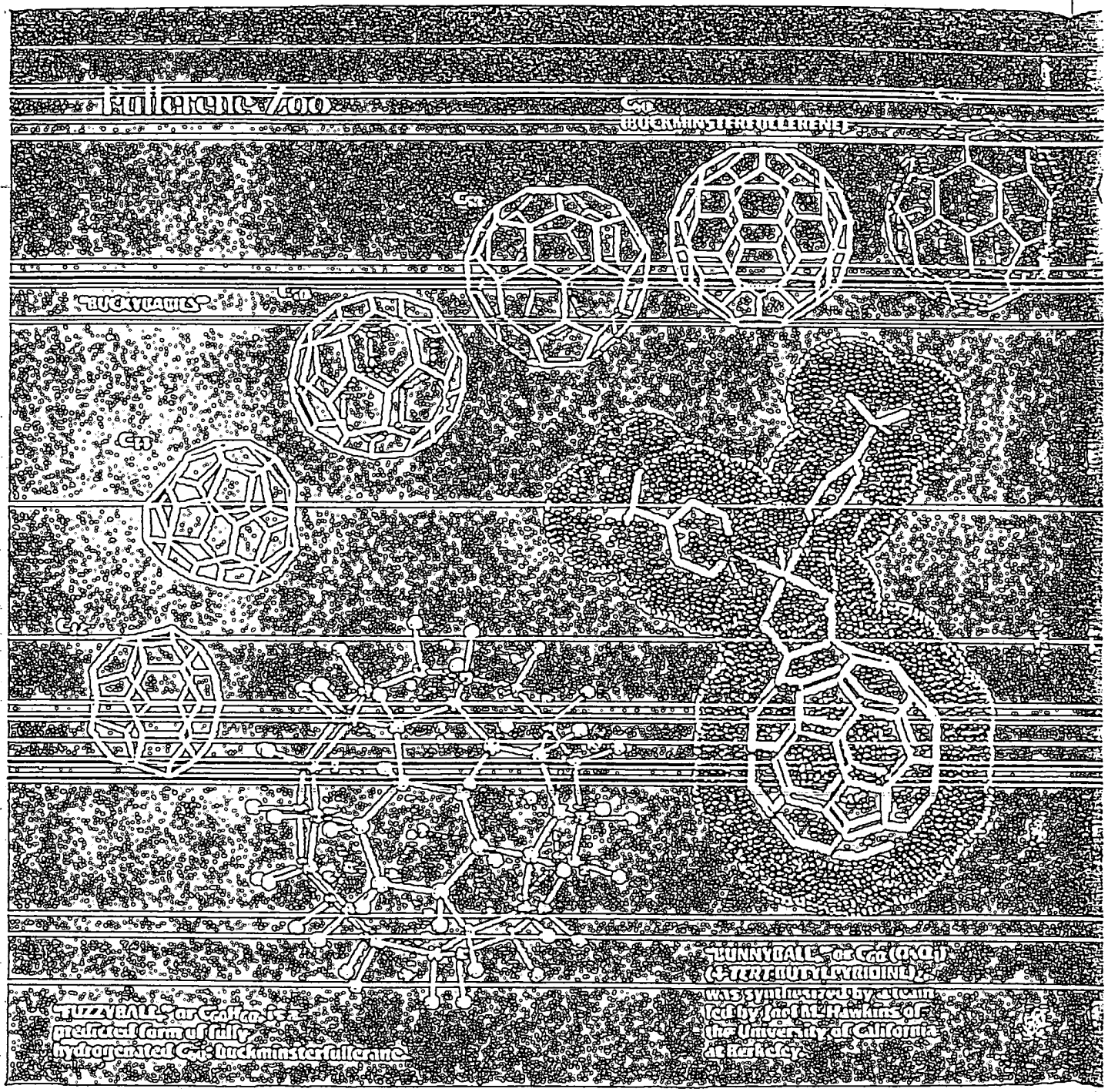
Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Perhaps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected C_{60} to be available in bulk anytime soon.

In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from observations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [*see bottom illustration on page 58*]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of

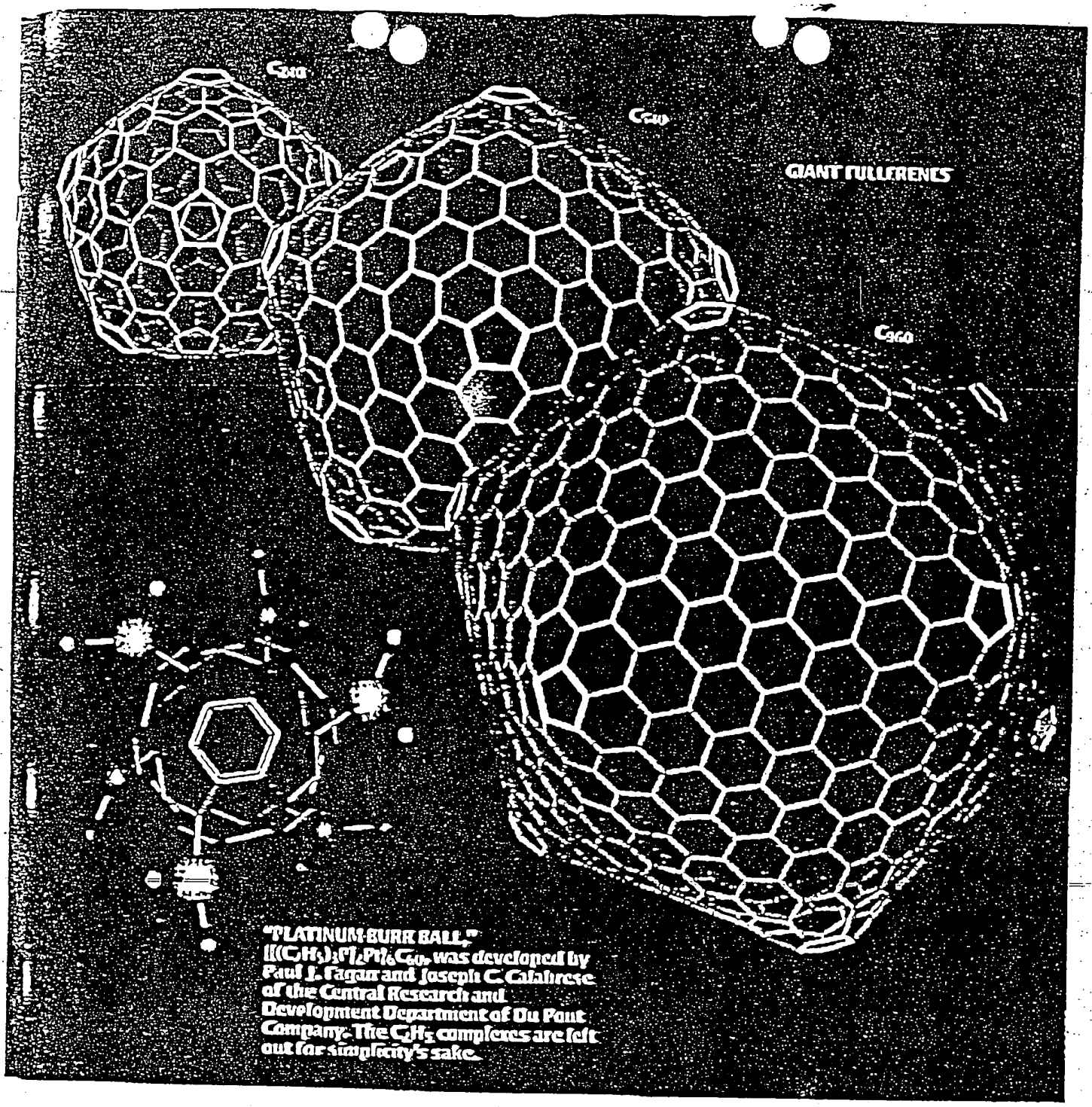




our discovery of C_{60} and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that C_{60} account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikeliness of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the C_{60} hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball C_{60}. These predictions held that of the 174 vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that C_{60} might be present in abundance.

Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-



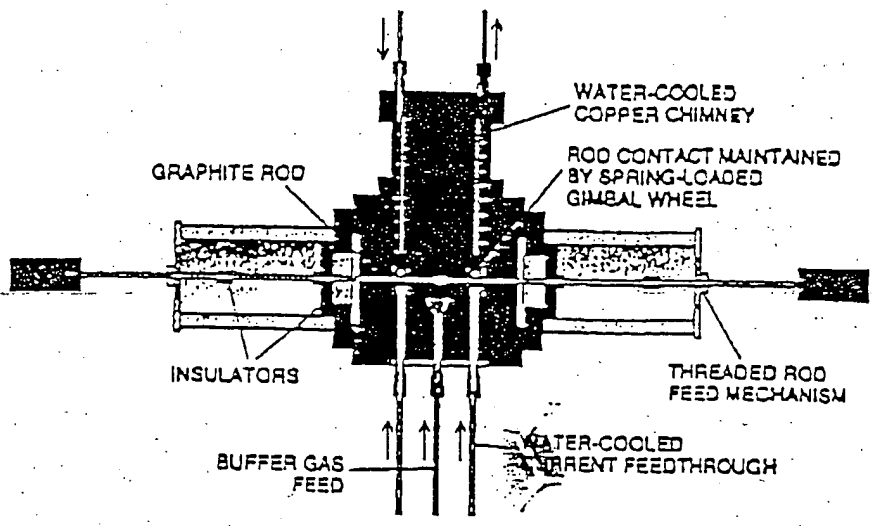
"PLATINUM-BURR BALL," $[(C_6H_5)_3P]_2Pt_6C_{60}$, was developed by Paul J. Fagan and Joseph C. Calabrese of the Central Research and Development Department of Du Pont Company. The C_6H_5 complexes are left out for simplicity's sake.

volved route. They prepared a sample from pure ^{13}C, a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of C_{60}. Because benzene molecules take the shape of a ring of carbon atoms, C_{60} would thus be seen as a kind of spherical benzene.

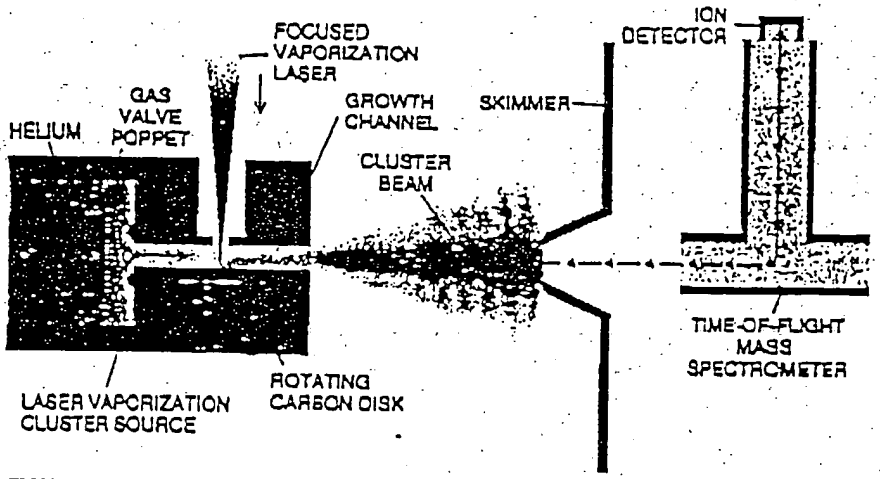
When the Kratschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials, which Kratschmer and Huffman christened "fullerite."

In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent C_{60} (the soccerball), 23 percent C_{70} (the rugby ball) and a grab bag of larger fullerenes.

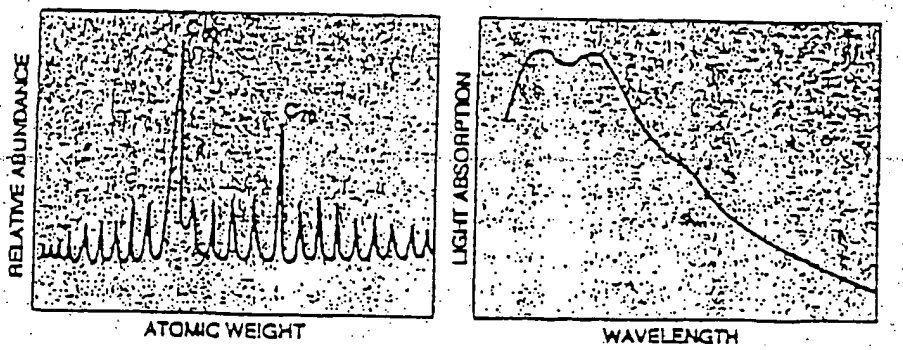
Here was a new form of pure, solid



FULLERENE FACTORY makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



CLUSTER GENERATOR designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



CRUCIAL GRAPHS: In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially C_{60}, suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain C_{60}.

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with hunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of C_{60} and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written [*see box on page 62*]. The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for C_{60} arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because C_{60} is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show.

more than 100 million times a second. The NMR experiments also dramatically verify that C_{70} has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when C_{60} molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect—C_{60} crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [*see illustration on page 62*]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of C_{60}. Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of C_{60}. In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [*see box on page 62*]—the manufacturing cost of C_{60} will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fail in the search for the yellow vial? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?

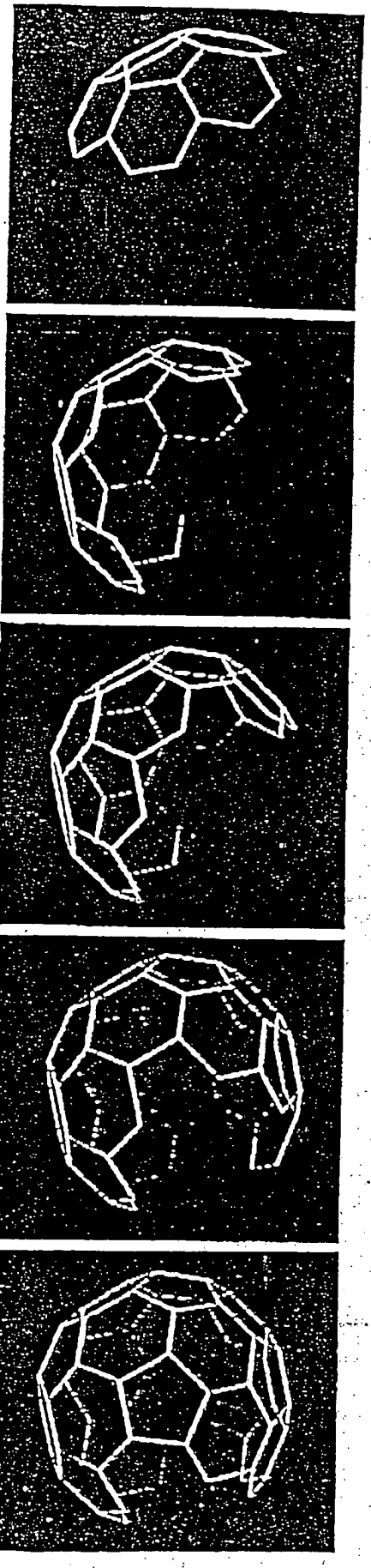
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cagelike structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of C_{60}. Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; SCIENTIFIC AMERICAN, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

Growth of a Buckyball



cally inert carrier gas, which carried vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members, C_{60} and C_{70}, were somewhat more abundant than their neighbors [*see bottom illustration on page 58*]. The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

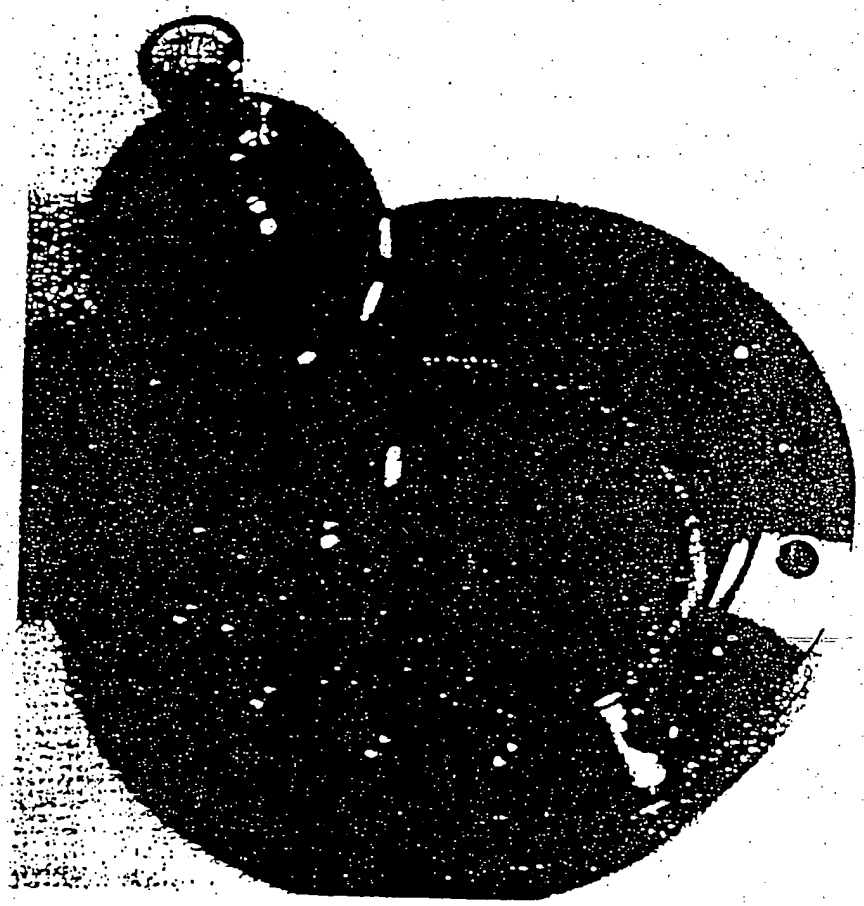
The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which C_{60} stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

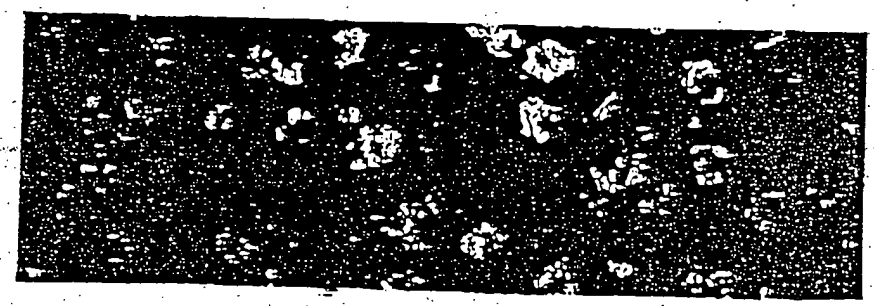
We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is C_{60}; the next is C_{70}. Although C_{71} and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained positio. This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF C_{60} depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.



FULLERENE CRYSTALS were produced by evaporating a benzene solution of C_{60} containing a significant admixture of C_{70}.

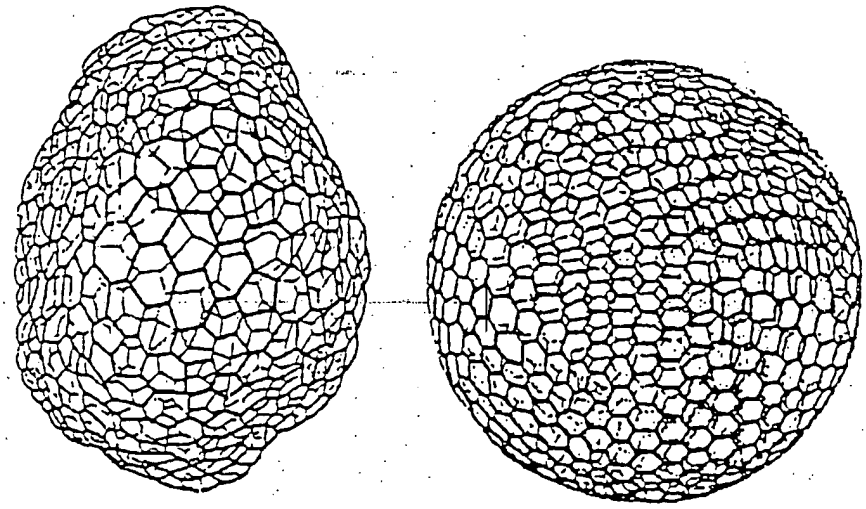
graphitic sheet structures as flat. After all, the sheets are certainly flat in a perfect crystal of graphite, and there is a huge class of very stable polycyclic aromatic hydrocarbons that are also flat (naphthalene and anthracene, for instance). But these free-floating graphitic sheets in the condensing carbon vapor have no atoms to tie up the dangling bonds on their edges. They therefore have little reason to remain flat. Indeed, the physical tendency to reach the lowest energy level available induces the sheets to eliminate their dangling bonds by curling up.

We discovered a strategy—the pentagon rule—according to which the sheets could accomplish this feat. The sheets rearrange their bonding so that pentagons are formed, causing the network to curve and permitting at least one good carbon-carbon bond to replace two dangling bonds. If some pentagons were good, more would be better. But we cautioned that it would be wise to avoid having two pentagons positioned so that they shared an edge, since this configuration is known to be rather unstable. If this process continues as the graphitic sheet grows, the network will naturally curl until the opposing edges meet to form the perfect soccerball structure. In this way, we argued in 1985, the formation of buckminsterfullerene from spontaneously condensing carbon vapor might not be so surprising after all.

Of course, there is no reason to expect that all growing graphitic sheets will close up—they merely have a theoretical propensity to do so. In reality, we expected clusters to grow too fast for imperfections to be corrected, so that the growing edge would typically overrun the opposite side, much like an overgrown toenail. Further growth would result in a spiraling nautilus-shaped structure that would prevent the growing edge from ever meeting its opposite, which would be hopelessly buried on the inside of the spiral.

This spiral shape seemed so interesting that we went on to suggest it may be formed in sooting flames and may in fact be the nucleus involved in the formation of soot. In this scenario, fullerenes like C_{60} and C_{70} are rather unlikely local stopping points in a curving, spiraling growth mechanism that ultimately results in soot.

Although this turned out to be a useful model, which within a few years led to the discovery that C_{60} and the other fullerenes are in fact abundant in all sooting flames, to some extent it misled us. Perfect closure need not always be that unlikely. Granted, the curving process is liable to be waylaid in a candle flame, where much hydrogen wanders around, tying up dangling bonds as it goes. These terminated dangling bonds would tend to frustrate the curving and closing mechanism.



LIVING FULLERENES: these radiolarians—protozoans having siliceous skeletons—appear in D'Arcy Thompson's 1917 classic, *On Growth and Form*.

But in a pure condensing carbon vapor one may be able to prolong the period in which the carbon nets remain open. If the temperature is kept high enough, the nets will effectively anneal, that is, they will adopt their most favored form by obeying the pentagon rule. Such conditions should thus produce a very high yield of C_{60}. This is what we believe Krätschmer and Huffman achieved. By using a simple, resistively heated graphite rod, they ensured that the concentration of small linear carbon radicals would be low and that the graphitic sheets would add these chains to their edges relatively slowly. The helium was critical, we believe, because it slowed migration of these chains away from the graphite rod. More chains lingered near the arc, which provided the heat they needed to continue to curve.

Not only was this line of reasoning available to us in 1985, it was a direct extension of the growth model we proposed at the time. Yet the yellow vial, so close to our grasp, eluded us because we did not think big. We were so intent on proving the existence of soccerball molecules that we asked no more of our model than that it rationalize tiny yields of C_{60}. Had we asked for more, had we considered the model's logical consequences, we would have—at least we should have—realized that we were heating and cooling the carbon too fast for it to anneal properly.

The solution would then have become obvious: the whole apparatus must be heated so that the laser-vaporized carbon plume expands further while it is still hot enough to anneal. Sure enough, when we finally did this in November 1990 by keeping the graphite target in an oven at 1,200 degrees C while passing helium over it slowly, a yellow-brown film of C_{60} and C_{70} rapidly sublimed on the surface of the oven. We found what we were looking for—five years late.

It appears, therefore, that a rather simple model explains the ready formation of this brand-new class of carbon molecules. Amazingly, C_{60} appears to result inevitably when carbon condenses slowly enough and at a high enough temperature. This discovery has come a bit later than it should have. But no matter: now we have it. And now the real fun can begin!

FURTHER READING

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SPACE, STARS, C60, AND SOOT. Harold Kroto in *Science*, Vol. 242, pages 1139–1145; November 25, 1988.

GREAT BALLS OF CARBON: THE STORY OF BUCKMINSTERFULLERENE. Richard E. Smalley in *The Sciences*, Vol. 31, No. 2, pages 22–28; March/April 1991.

STRUCTURE OF SINGLE-PHASE SUPERCONDUCTING K_3C_{60}. Peter W. Stephens, Laszlo Mihaly, Peter L. Lee, Robert L. Whetten, Shiou-Mei Huang, Richard Kaner, François Deiderich and Karoly Holczer in *Nature*, Vol. 351, No. 6328, pages 632–634; June 20, 1991.

FULLERENES C_{60} AND C_{70} IN FLAMES. Jack B. Howard, J. Thomas McKinnon, Yakov Makarovsky, Arthur L. Lafleur and M. Elaine Johnson in *Nature*, Vol. 352, No. 6331, pages 139–141; July 11, 1991.

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire, these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams. Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes.

Chemists are conditioned to think of

Fullerene Electronics

Currently the most technologically interesting properties of bulk C_{60} are electronic: in various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when C_{60} molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk C_{60} has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope, C_{60} with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that K_3C_{60} is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

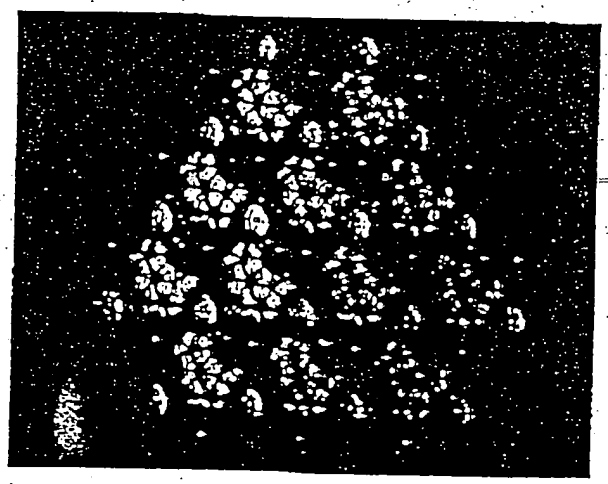
The Bell Labs team further discovered that this K_3C_{60} metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium–doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

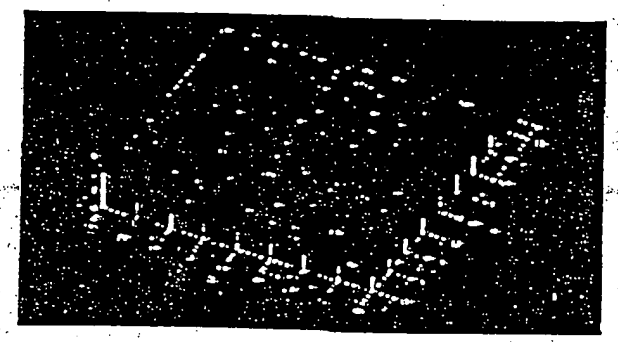
The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered C_{60} films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the K_3C_{60} superconductor can also be made (*see micrograph at right*), and the interface between the C_{60} crystalline film and the K_3C_{60} material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to learn how to dope them selectively to make *n*-type and *p*-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the C_{60} cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk C_{60} seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparalleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ($C_{60}F_{60}$). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.





SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of K_3C_{60} (*diagram*), producing a crystal that can be grown on a gallium arsenide substrate (*scanning tunneling micrograph*).

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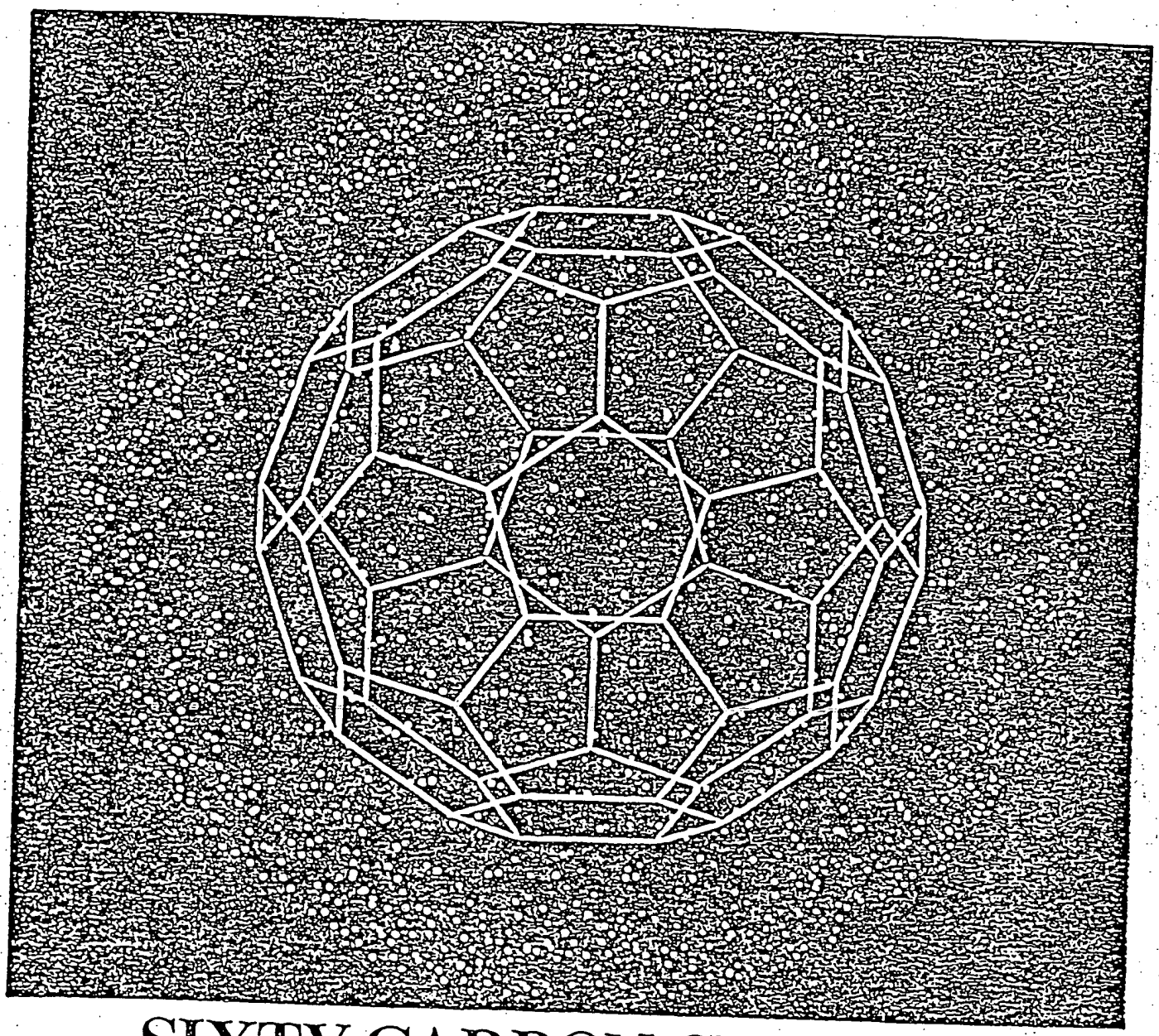

SIXTY-CARBON CLUSTER

AUTUMN BOOKS

Harvey Brooks
(transformation of MIT)

P. N. Johnson-Laird
(brain and mind)

Anthony W. Clare
(psychoanalysis as religion)

A. O. Lucas
(war on disease)

Hendrik B. G. Casimir
(physics and physicists)

Gordon Thompson
(dimensions of nuclear proliferation)

Jacques Ninio
(origins of life)

Edward Harrison
(steps through the cosmos)

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C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

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During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously[2-5].

The vaporization of carbon has been studied previously in a very similar apparatus[6]. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the C_{60} peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the C_{60} peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which C_{60} is totally dominant. In Fig. 3*c*, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38–120 atoms resulted. The C_{60} peak was largest but not dominant. In Fig. 3*b*, the vaporization laser was fired at the time of maximum helium density; the C_{60} peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C_{70}. In Fig. 3*a*, the conditions were similar to those in Fig. 3*b* but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by C_{60}, in fact more than 50% of the total large cluster abundance is accounted for by C_{60}; the C_{70} peak has diminished in relative intensity compared with C_{60}, but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar graphite fused six-membered ring structure. We believe that the distribution in Fig. 3*c* is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

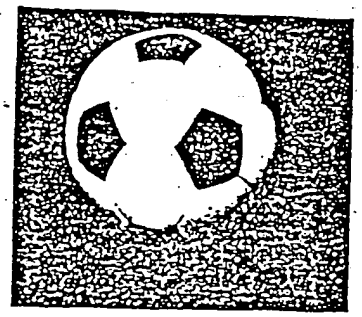

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp^2 valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C_{60} molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms[8].

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

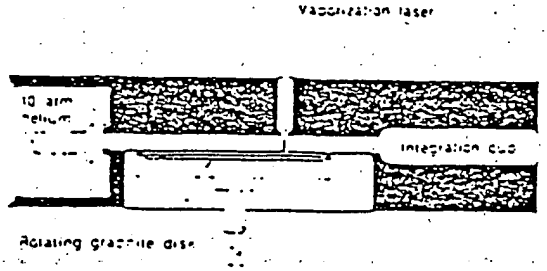

Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam (30–40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle, striking a graphite disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

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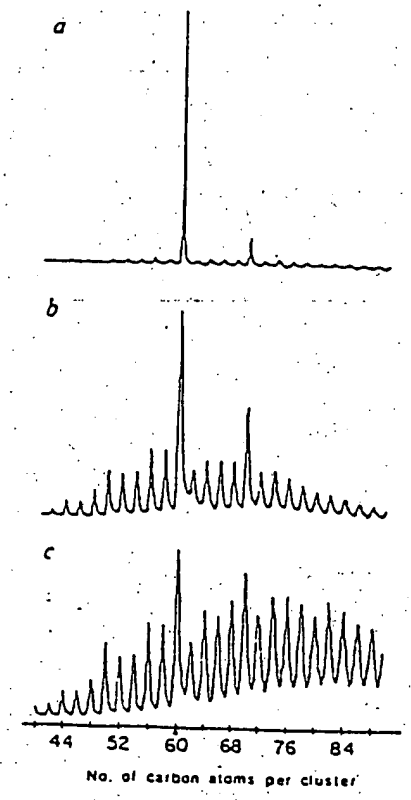

Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In *c*, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in *b* was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in *a* was obtained by maximizing these cluster thermalization and cluster-cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively, C_{60} or a derivative might be the carrier of the diffuse interstellar lines[9].

If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C_{60} derivatives of many kinds—such as C_{60} transition metal compounds, for example, $C_{60}Fe$ or halogenated species like $C_{60}F_{60}$ which might be a super-lubricant. We also have evidence that an atom (such as lanthanum[2] and oxygen[1]) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this C_{60} species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

We thank Frank Tittel, Y. Liu and Q. Zhang for helpful discussions, encouragement and technical support. This research was supported by the Army Research Office and the Robert A. Welch Foundation, and used a laser and molecular beam apparatus supported by the NSF and the US Department of Energy. H.W.K. acknowledges travel support provided by SERC, UK. J.R.H. and S.C.O'B. are Robert A. Welch Predoctoral Fellows.

Received 13 September; accepted 18 October 1985.

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The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"

Press release

The Fullerene Gallery

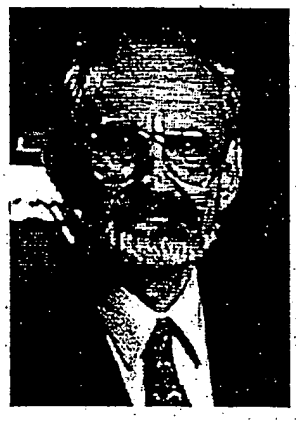
Robert F. Curl, Jr.

USA

Rice University
Houston, USA

1933 -

Autobiography



Sir Harold W. Kroto

U.K.

University of Sussex,
Brighton, U.K.

1939 -

Autobiography

Richard E. Smalley

USA

Rice University,
Houston, USA

1943 -

Autobiography

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Press Release: The 1996 Nobel Prize in Chemistry

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

9 October 1996

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor **Robert F. Curl, Jr.**, Rice University, Houston, USA,
Professor **Sir Harold W. Kroto**, University of Sussex, Brighton, U.K., and
Professor **Richard E. Smalley**, Rice University, Houston, USA,

for their discovery of fullerenes.

Note: This document is made for Netscape 2.0 or later, and some of the chemical formulas might not appear as intended using other browsers.

The discovery of carbon atoms bound in the form of a ball is rewarded

New forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells was discovered in 1985 by **Robert F. Curl, Harold W. Kroto** and **Richard E. Smalley**. The number of carbon atoms in the shell can vary, and for this reason numerous new carbon structures have become known. Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon(VI). The latter two were discovered in 1968 and 1972.

Fullerenes are formed when vaporised carbon condenses in an atmosphere of inert gas. The gaseous carbon is obtained e.g. by directing an intense pulse of laser light at a carbon surface. The released carbon atoms are mixed with a stream of helium gas and combine to form clusters of some few up to hundreds of atoms. The gas is then led into a vacuum chamber where it expands and is cooled to some degrees above absolute zero. The carbon clusters can then be analysed with mass spectrometry.

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms, C_{60}, were the most abundant. They found high stability in C_{60}, which suggested a molecular structure of great symmetry. It was suggested that C_{60} could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodetic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure *buckminsterfullerene* after him.

The discovery of the unique structure of the C_{60} was published in the journal *Nature* and had a mixed reception - both criticism and enthusiastic acceptance. No physicist or chemist had expected that carbon would be found in such a symmetrical form other than those already known. Continuing their work during 1985-90, Curl, Kroto and Smalley obtained further evidence that the proposed structure ought to be correct. Among other things they succeeded in identifying carbon clusters that enclosed one or more metal atoms. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C_{60} by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent. They obtained a mixture of C_{60} and C_{70}, the structures of which could be determined. This confirmed the correctness of the C_{60} hypothesis. The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}. New substances were produced from these compounds, with new and unexpected properties. An entirely new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.

Background

Many widely diverse research areas coincide in the discovery of the fullerenes. **Harold W. Kroto** was at the time active in microwave spectroscopy, a science which thanks to the growth of radioastronomy can be used for analysing gas in space, both in stellar atmospheres and in interstellar gas clouds. Kroto was particularly interested in carbon-rich giant stars. He had discovered and investigated spectrum lines in their atmospheres and found that they could be ascribed to a kind of long-chained molecule of only carbon and nitrogen, termed cyanopolyynes. The same sort of molecules is also found in interstellar gas clouds. Kroto's idea was that these carbon compounds had been formed in stellar atmospheres, not in clouds. He now wished to study the formation of these long-chain molecules more closely.

He got in touch with **Richard E. Smalley**, whose research was in cluster chemistry, an important part of chemical physics. A cluster is an aggregate of atoms or molecules, something in between microscopic particles and macroscopic particles. Smalley had designed and built a special *laser-supersonic cluster beam apparatus* able to vaporise almost any known material into a plasma of atoms and study the design and distribution of the clusters. His paramount interest was clusters of metal atoms, e.g. metals included in semiconductors, and he often performed these investigations together with **Robert F. Curl**, whose background was in microwave and infra-red spectroscopy.

Atoms form clusters

When atoms in a gas phase condense to form clusters, a series is formed where the size of the clusters varies from a few atoms to many hundreds. There are normally two size maxima visible in the distribution curve, one around small clusters and one around large. It is often found that cer-tain cluster sizes may dominate, and the number of atoms in these is termed a "magic number", a term borrowed from nuclear physics. These dominant cluster sizes were assumed to have some special property such as high symmetry.

Fruitful contact

Through his acquaintanceship with Robert Curl, Kroto learned that it should be possible to use Smalley's instrument to study the vaporisation and cluster formation of carbon, which might afford him evidence that the long-carbon-chain compounds could have been formed in the hot parts of stellar atmospheres. Curl conveyed this interest to Smalley and the result was that on 1 September 1985 Kroto arrived in Smalley's laboratory to start, together with Curl and Smalley, the experiments on carbon vaporisation. In the course of the work it proved possible to influence drastically the size distribution of the carbon clusters where, predominantly, 60 appeared as a magic number but also 70 (Fig. 1). The research group

now got something else to think about. Instead of long carbon chains, the idea arose that the C_{60} cluster could have the structure of a truncated (cut off) icosahedron (Fig. 2) since its great stability was assumed to correspond to a closed shell with a highly symmetrical structure. C_{60} was given a fanciful name, buckminsterfullerene, after the American architect R. Buckminster Fuller, inventor of the geodesic dome. This hectic period ended on 12 September with the despatch of a manuscript entitled *C_{60}: Buckminsterfullerene* to *Nature*. The journal received it on 13 September and published the article on 14 November 1985.

Sensational news

For chemists the proposed structure was uniquely beautiful and satisfying. It corresponds to an aromatic, three-dimensional system in which single and double bonds alternated, and was thus of great theoretical significance. Here, moreover, was an entirely new example from a different research tradition with roots in organic chemistry: producing highly symmetrical molecules so as to study their properties. The Platonic bodies have often served as patterns, and hydrocarbons had already been synthesised as tetrahedral, cubic or dodecahedral (12-sided) structures.

Carbon atoms per cluster

Fig. 1
Using mass spectroscopy it was found that the size distribution of carbon clusters could be drastically affected by increasing the degree of chemical "boiling" in the inlet nozzle to the vacuum chamber. Clusters with 60 and 70 carbon atoms could be produced. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Fig. 2
Models of the structures of C_{60}. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Further investigations

To gain further clarity Curl, Kroto and Smalley continued their investigations of C_{60}. They attempted to make it react with other compounds. Gases such as hydrogen, nitrous oxide, carbon monoxide, sulphur dioxide, oxygen or ammonia were injected into the gas stream, but no effect on the C_{60} peak recorded in the mass spectrometer could be demonstrated. This showed that C_{60} was a slow-reacting compound. It also turned out that all carbon clusters with an even number of carbon atoms from 40-80 (the interval that could be studied) reacted equally slowly. Analogously with C_{60} all these should then correspond to entirely closed structures, resembling cages. This was in agreement with Euler's law, a mathematical proposition which states that for any polygon with *n* edges, where *n* is an even number greater than 22, at least one polyhedron can be constructed with 12 pentagons and (*n*-20)/2 hexagons, which, in simple terms, states that it is possible with 12 pentagons and with none or more than one hexagon to construct a polyhedron. For large *n* many different closed structures can occur, thus also for C_{60}, and it was presumably the beautiful symmetry of the proposed structure that gave it the preference.

The combination of chemical inertia in clusters with even numbers of carbon atoms and the possibility that all these could possess closed structures in accordance with Euler's law, led to the proposal that all these carbon clusters should have closed structures. They were given the name fullerenes and conceivably an almost infinite number of fullerenes could exist. The element carbon had thus assumed an almost infinite number of different structures.

C_{60} and metals

New experiments were rapidly devised to test the C_{60} hypothesis. Since the C_{60} structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. A graphite sheet was soaked with a solution of a metal salt (lanthanum chloride, $LaCl_3$) and subjected to vaporisation-condensation experiments. Masspectroscopic analysis of the clusters formed showed the presence of $C_{60}La^+$. These proved to be photoresistant, i.e. irradiation with intense laser light did not remove the metal atoms. This reinforced the idea that metal atoms were captured inside the cage structure.

The possibility of producing clusters with a metal atom enclosed gave rise to what was termed the "shrink-wrapping" experiment. Ions of one and the same size or at least similar sizes were gathered in a magnetic trap and subjected to a laser pulse. It then turned out that the laser beam caused the carbon cage to shrink by 2 carbon atoms at a time: at a certain cage size, when the pressure on the metal atom inside

became too great, the fragmentation ceased. The shell had then shrunk so that it fitted exactly around the metal atom. For $C_{60}Cs^+$ this size was at $C_{48}Cs^+$, for $C_{60}K^+$ it was at $C_{44}K^+$ and for C_{60}^+ at C_{32}^+.

Further strong evidence gave rise to new chemistry

At the end of the 1980s, strong evidence was available that the C_{60} hypothesis was correct. In 1990 the synthesis of macroscopic quantities of C_{60} through carbon arc vaporisation between two graphite electrodes permitted the attainment of full certainty - the whole battery of methods for structure determination could be applied to C_{60} and other fullerenes and completely confirmed the fullerene hypothesis. As opposed to the other forms of carbon the fullerenes represent well-defined chemical compounds with in some respects new properties. A whole new chemistry has developed to manipulate the fullerene structure, and the properties of fullerenes can be studied systematically. It is possible to produce superconducting salts of C_{60}, new three-dimensional polymers, new catalysts, new materials and electrical and optical properties, sensors, and so on. In addition, it has been possible to produce thin tubes with closed ends, nanotubes, arranged in the same way as fullerenes. From a theoretical viewpoint, the discovery of the fullerenes has influenced our conception of such widely separated scientific problems as the galactic carbon cycle and classical aromaticity, a keystone of theoretical chemistry. No practically useful applications have yet been produced, but this is not to be expected as early as six years after macroscopic quantities of fullerenes became available.

Further reading

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Hugh Aldersey-Williams, *The Most Beautiful Molecule: An Adventure in Chemistry*, Aurum Press, London, 1995, IX + 340 pp.

Robert F. Curl and Richard E. Smalley, *Probing C_{60}*, Science, 18 Nov. 1988 Vol. 242

Harold Kroto, *Space, Stars, C_{60} and Soot*, Science, 25 Nov. 1988 Vol. 242

H.W. Kroto, A.W. Allaf, and S.P. Balm, *C_{60}: Buckminsterfullerene*, American Chemical Society, 1991

Richard E. Smalley, *Great Balls of Carbon; The Story of Buckminsterfullerene*, The Sciences, March/April 1991

The All-Star of Buckyball; Profile: Richard E. Smalley, Scientific American, September 1993

Rudy M. Baum, *Commercial Uses of Fullerenes and Derivatives Slow to Develop*, News Focus, Nov. 22, 1993 C&EN

Hargittai, Istv(SIGMA)n, *Discoverers of Buckminsterfullerene*, The Chemical Intelligencer, Springer-Verlag, New York, 1995

Robert F. Curl Jr., was born in 1933 in Alice, Texas, USA: Ph.D. in chemistry in 1957 at University of California, Berkeley, USA. Curl has since 1958 worked at Rice University, where he has been a professor since 1967.

Professor Robert F. Curl Jr.
Department of Chemistry
Rice University
P.O. Box 1892
Houston, TX 77251, USA

Sir Harold W. Kroto was born in 1939 in Wisbech, Cambridgeshire, UK. He obtained his Ph.D. in 1964

at the University of Sheffield, UK. In 1967 he moved to the University of Sussex, where he still works. In 1985 he became Professor of Chemistry there and in 1991 Royal Society Research Professor.

Professor Sir Harold W. Kroto
School of Chemistry and Molecular Sciences
University of Sussex
Brighton, Sussex BN1 9QJ, UK

Richard E. Smalley was born in 1943 in Akron, Ohio, USA. Ph.D. in chemistry 1973 at Princeton University, USA. Professor of Chemistry at Rice University since 1981 and also Professor of Physics at the same university since 1990. Member of the National Academy of Sciences in the USA and other bodies.

Professor Richard E. Smalley
Department of Chemistry
Rice University
P.O. Box 1892
Houston, TX 77251, USA

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PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Huffman, et al. Examiner:

Serial No.: 07/580,246 Art Unit: 1103

Filed: October 22, 1991 Docket: 7913Z

For: NEW FORM OF CARBON

Assistant Commissioner of Patents
Washington, DC 20231

DECLARATION OF HAROLD W. KROTO UNDER 37 C.F.R. §1.132

Sir:

I, Harold W. Kroto, Ph.D., declare and say as follows:

1. I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom. For the convenience of the U.S. Patent Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2. I am intimately familiar with the literature concerning and was personally involved in the search for C_{60} and the greater fullerene family. For convenience, one may refer particularly to our review of the literature through 1990 described in an article entitled "C_{60} Buckminsterfullerene" in Chem. Rev. 1991. 1231-1235 attached hereto as Exhibit 2 and for my personal involvement in the research effort in my article entitled "C_{60}: Buckminsterfullerene, the Celestial Sphere that Fell to Earth" in Angewandte Chemie I.E.E. 1992, 31, 111-129 attached as Exhibit 3. I therefore believe it is fair to say that I am among the recognized experts in the subject of fullerenes.

3. I have reviewed the above-identified application. The application teaches in clear detail to the skilled artisan the preparation of fullerenes, including C_{60}, in quantities that were never recognizably achieved before the discovery by Huffman and Kratschmer described in the application. Specifically, the application describes the production of C_{60} and C_{70} in macroscopic amounts, i.e., amounts that could be seen with the naked eye. In addition, the application describes the preparation of substantially pure C_{60} and C_{70} and crystalline C_{60} and C_{70}. Their discovery for the first time permitted researchers to confirm the existence and structure of fullerenes including subjecting them to general testing of their detailed properties and characteristics, which had heretofore only been projected based upon educated speculation and calculation, grounded upon circumstantial evidence of their existence.

4. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of C_{60} and C_{70} by the methods described in the above-identified application is recognized by the knowledgeable scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as C_{60} could be achieved by these methods, as it was expected that no more than < 1/10000 parts of fullerenes would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

5. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed,

especially in hindsight, their discovery was quite remarkable. This is readily appreciated if one considers the historical perspective. Ever since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 3, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my knowledge, one group, Huffman and Kratschmer, were the first to find a methodology capable of producing and isolating fullerenes, such as C_{60}, in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

6. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical prediction about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating more than four thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes.

7. I have been ask to review the following two articles:

(a) "Fullerenes from the Geological Environment" by Peter Buseck, et al. in Science 1992, 257, 215-217 ("Buseck, et al.")

(b) "....and shower the Earth with buckyballs", by Jeff Hecht, New Scientist 1994 16 ("Hecht").

8. I have noted that both articles were published after Drs. Huffman and Kratschmer published their paper in Nature

1990, 347, 354-358, describing the specific production of macroscopic quantities of C_{60} and C_{70}, their isolation and characterization including the UV spectra of the C_{60}. A copy of this article is attached hereto as Exhibit 6.

9. Those facts in paragraph 8 are important since at the time of the publication of the articles cited in Paragraph 7 hereinabove, the skilled artisan in the field of fullerenes had samples of C_{60} and C_{70} in his possession. Unless special precautions are taken, it is very easy to contaminate samples having alleged trace amounts of C_{60} and C_{70} with these fullerenes. Contamination of the samples with fullerenes would obscure the results when working with low concentrations of C_{60} and C_{70}.

10. The Buseck, et al. article alleges that C_{60} and C_{70} were found in minute amounts in fissures in a rock identified as shungite, a carbonaceous rock found near the town of Shunga, in Karelia, Russia. It also alleges that the fullerenes are unevenly distributed in the fissures.

11. This article was and is still met with a certain amount of skepticism by the scientific community and the findings therein are highly controversial, even today. Many scientists tried to reproduce their results, but were unsuccessful. See, for example, "TECHNICAL COMMENTS" "Origins of Fullerenes in Rocks", published in Science 1995, 268, 1634-1635 attached hereto as Exhibit 7 wherein Ebbesen, et al. indicate that they were unable to obtain any fullerene from their sample of shungite.

12. I also am not completely convinced that the conclusions in the Buseck et al. article regarding the presence of fullerenes in shungite are correct. I also was able to obtain shungite rock from Russia, but was unable to find any evidence of the presence of C_{60} and C_{70} in these samples.

13. Another problem with the methods disclosed in the Buseck et al. article was the use of the laser technique to allegedly detect the C_{60} and C_{70} in their sample of shungite. As the skilled artisan is well aware, laser under certain conditions has been used to generate fullerenes. Even though reasonable efforts were made to allay suspicion in this regard, the paper does not entirely eliminate the possibility that C_{60} and C_{70} might have been produced during the sampling phase.

14. I also have queries about their findings for other reasons; I would have expected the whole range of related fullerenes to be found with any naturally produced C_{60} and C_{70}. Yet, Buseck, et al. did not report any such finding.

15. The Hecht article is a report by a third party, alleging that Dieter Heymann found C_{60} in New Zealand Clay. However, the article does not present any data or evidence of Heymann in support of the allegations therein.

16. The C_{60} and C_{70} described in these articles were allegedly found in trace amounts, in parts per billion. There are no large pockets of fullerenes, e.g., C_{60} and C_{70}, and where they are reported to be found, they are not reported to be found in macroscopic amounts. The amounts of C_{60} and C_{70} reportedly found are too small to be useful to the skilled artisan. It does not seem feasible that macroscopic amounts of C_{60} and C_{70} will be produced from mining these rocks.

17. Furthermore, when reportedly found in the natural environment, the C_{60} and C_{70} are never found as isolates. They are reported to be found as a part of a larger geological sample and are thus very impure.

18. Furthermore, the C_{60} and C_{70} reportedly found are alleged to be distributed in a matrix. It is my opinion that crystalline C_{60} and C_{70} have not been found in nature.

19. After reading these articles, I can say, without any reservation, that macroscopic amounts of C_{60} and C_{70} are not naturally found.

20. It is also important to note that there may be some confusion regarding the use of the term "soot". The soot referred to in the Huffman and Kratschmer application, which I shall call "fullerene black", is prepared by vaporization of graphite, in accordance with the procedure described therein. It contains the fullerenes, which are extracted therefrom. The "soot" in the Hecht article is believed to be derived from global forest fires at the end of the Cretaceous period. It is quite distinct from the "fullerene black." The "fullerene black" is also distinct from the soot produced during combustion of carbon in oxygen. The "fullerene black" in the Huffman and Kratschmer application is man-made and is not naturally produced.

21. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that any false statements and the like so made are punishable by fine or imprisonment or both under section 1001, Title 18 of United States Code and that such willful false statements may jeopardize the validity of any application or any patent issuing thereon.

Dated 27/7/95

Harold W. Kroto, Ph. D.

CURRICULUM VITAE

Harold Kroto FRS
Royal Society Research Professor

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Born 7th Oct 1939 Wisbech, Cambridgeshire, England.

Education

1947-58 Bolton School, Bolton, Lancashire.

1958-61 BSc, University of Sheffield, 1st class honours degree (Chemistry)

1961-64 PhD, University of Sheffield *Electronic Spectroscopy of Unstable Molecules*
Supervisor: R N Dixon FRS (now Professor, Bristol)

1964-65 Postdoctoral Fellow, National Research Council (Ottawa) with D A Ramsay FRS

1965-66 Postdoctoral Fellow, National Research Council (Ottawa) with C C Costain

1966-67 Member of Technical Staff, Bell Telephone Laboratories, Murray Hill, N.J. (with Y H Pao, now at Case Western Reserve and D P Santry now at McMaster U)

University Career (University of Sussex 1967-)

1967-68 Tutorial Fellow.
1968-78 Lecturer
1978-85 Reader
1985-91 Professor
1991- Royal Society Research Professor.

Extra-university administration

SRC Millimetre Wave Telescope Sub-Committee 1977-81
SERC Millimetre Wave Telescope Users'Committee 1981-85
SERC Physical Chemistry Subcommittee 1987-90
SERC Synchrotron Radiation Facility Committee 1987-90
SERC Chemistry Committee 1988-91
IAU Sub-group on Astrophysical Chemistry 1987-
MBI Advisory Board of the Max Born Institute (Berlin) 1993-

Meeting (director, organiser or co-orgnaisor)

Brioni International Conferences 1988, 1990, 1993, ...
Royal Society Discussion Meeting 1992
Fullerene Symposium 1993 (Santa Barbara)
Cursos de Verano (El Escorial) *Fullerenos* 1994

Editorial Boards

Chemical Society Reviews 1986- (Chairman 1990-)
Zeitschrift fur Physik D (Atoms Molecules and Clusters) 1992-
Carbon (1992-)
J. Chem. Soc. Chem. Comm. (1993-)

Research Details

University of Sheffield

1961-64 PhD in Free radical spectroscopy by flash photolysis

National Research Council

1964-65 Free radical spectroscopy by flash photolysis
1965-66 Microwave Spectroscopy

Bell Telephone Laboratories

1966-67 Raman Spectroscopy of Liquids, Quantum Chemistry

University of Sussex

1967-72 Free radical spectroscopy/flash photolysis
1967-73 Liquid phase interactions/Raman Spectroscopy
1970- Unstable species/Microwave Spectroscopy
1972-90 Unstable species/Photoelectron Spectroscopy
1976- Interstellar Molecules/Radioastronomy
1983-90 Unstable species/Fourier Transform IR Spectroscopy
1985- Cluster Studies/Carbon, Metals
1990- Fullerene Chemistry, Carbon nanostructures

Temporary Appointments (Visiting Professorships etc)

1974 Visiting Associate Professor, UBC Vancouver (3 months)
1976 Visiting Scientist, NRC Ottawa (3 wks)
1978 Visiting Scientist, NRC Ottawa (3 wks)
1981 Visiting Professor, USC (3 months).
1983 British Council Visitor, Inst Rudjer Boskovic (Zagreb)
1987 CNRS (1 month) Univ Paris Sud (Orsay)
1988- Visiting Professor UCLA (Astronomy)

Extramural Activities

Sport

Tennis and Squash for Sheffield University (1959-1964).
University Athletics Union Finalists - Tennis (1962 and 1963)
President of Athletics Council, Sheffield University (1963-64)

Graphic Art, Design, Television Film

Art Editor *Arrows* Sheffield University Arts Magazine 1962-64
Winner of *Sunday Times* Book Jacket Design Competition 1963
Editor, design and layout of *Chemistry at Sussex*
featured in *Modern Publicity 1979* (international annual of Graphic Design)
Publicity and logos for Chemical Society Meetings
Logo, letterheads for Science and Engineering at Sussex

Publicity, logo, letterheads, poster for BA Meeting 1983
New Scientist BA Advertisement
Logo and letterhead for Inorganic Biochemistry Discussion Group
Logo and letterhead 1990 for *Venture Research International*
(Formerly *BP Venture Research*)
New Cover design and layout for *Chemical Society Reviews*

Chairman of Board of *VEGA SCIENCE TRUST*
Executive producer of five 1-hour Television Films of Royal Institution Discourses for Vega/BBCSelect

Miscellaneous

1981-82	Tilden Lecturer (Royal Society of Chemistry)
1990	Elected Fellow of the Royal Society
1991-	Royal Society Research Professorship
1992	International Prize for New Materials (American Physical Society, R F Curl and R E Smalley)
1992	Italgas Prize for Innovation in Chemistry
1992	Université Libre de Bruxelles (DHC)
1992	University of Stockholm (PhDHC)
1992	Longstaff Medal 1993 (Royal Society of Chemistry)
1992	Academia Europaea (Member)
1993	University of Limburg(DHC)
1994	Hewlett Packard Europhysics Prize (with D R Huffman, W Krätschmer and R E Smalley)
1994	Moet Hennessy*Louis Vuitton *Science pour l'Art* Prize

RESEARCH

Main research areas:

I Spectroscopy of Unstable Species and Reaction Intermediates
(Infrared, Photoelectron, Microwave and Mass Spectrometry)

II Cluster Science
(Carbon and Metal Clusters, Microparticles, Nanofibres)

III Fullerenes
(Chemistry, Physics and Materials Science)

IV Astrophysics
(Interstellar Molecules and Circumstellar Dust)

Research Highlights:

a) Synthesis in 1976 of the first phoaphaalkenes (compounds containing the free carbon phosphorus double bond) in particular $CH_2=PH$ (with N P C Simmons and J F Nixon, Sussex). Refs 1,7.

b) Synthesis in 1976 of the first analogues of HCP, the phosphaalkynes which contain the carbon phoshorus triple bond - in particular CH_3CP (with N P C Simmons and J F Nixon, Sussex), Refs 2,7.

c) The discovery (1976-8) of the cyanopolyynes, HC_nN (n = 5,7,9), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, Refs 3,7.

d) The discovery of C_{60}: Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), Refs 8,13,15.

e) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), Ref 9

f) The prediction that C_{60} should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) Ref 10

g) The explanation of why C_{70} is the second stable fullerene (after C_{60}) and the discovery of the *Pentagon Isolation Rule* as a criterion for fullerene stability in general (Refs 11,13,15)

h) The prediction of the tetrahedral structure of C_{28} and the possible stability of "tetravalent" derivatives such as $C_{28}H_4$ Refs 11,15.

i) The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), Refs 12,13.

j) The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C_{60} from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs 14,15.

k) The chromatographic separation/purification of C_{60} and C_{70} and ^{13}C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs 14,15.

PUBLICATIONS

180 research papers. One book "Molecular Rotation Spectra" (Wiley 1975) - reprinted with a new preface by Dover 1992.

Main Publications

1) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospha-alkenes $CF_2=PH$, $CH_2=PCl$ and $CH_2=PH$', *J.C.S. Chem. Comm.*, 513-515 (1976).

2) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne, CH_3CP, by microwave spectroscopy', *Chem. Phys. Letts.*, **42**, 460-461 (1976).

3) A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne, HC_5N', *J. Mol. Spectrosc.*, **62**, 175-180 (1976).

4) L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', *Astrophys. J.*, **205**, L173-175 (1976).

5) H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, 'The Detection of Cyanohexatriyne, HC_7CN, in Heiles' Cloud 2', *Astrophysics J.*, **219**, L133-L137 (1978).

6) N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of HC_9N in Interstellar Space', *Astrophys. J.*, **223**, L105-107 (1978).

7) H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; *Chem. Soc. Revs.*, **11**, 435-491 (1982).

8) H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, 'C_{60}: Buckminsterfullerene', *Nature*, **318**(No.6042), 162-163,(1985)

9) J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, H W Kroto, F K Tittel and R E Smalley 'Lanthanum Complexes of Spheroidal Carbon Shells', *J. Am. Chem. Soc.*, **107**, 7779-7780 (1985).

10) Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley. 'Reactivity of large carbon clusters Spheroidal Carbon Shells and their possible relevance to the formation and morphology of soot', *J. Phys. Chem.*, **90**, 525-528 (1986)

11) H W Kroto, 'The Stability of the Fullerenes C_n (n = 24, 28, 32, 50, 60 and 70)', *Nature* 329, 529-531 (1987)

12) H W Kroto and K McKay, 'The Formation of Quasi-icosahedral Spiral Shell Carbon Particles' *Nature*, 331, 328-331 (1988)

13) H W Kroto "Space, Stars, C_{60} and Soot", *Science*, **242**, 1139-1145 (1988)

14) R Taylor, J P Hare, A K Abdul-Sada, and H W Kroto, "Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70}: The Third Form of Carbon." *J. Chem. Soc. Chem. Commun.*, 1423-1425 (1990)

15) H W Kroto "C_{60}: Buckminsterfullerene, the Celestial Sphere that Fell to Earth", *Angewandte Chemie* **31**, 111-129 (1992)

SYMPOSIUM LECTURES and SEMINARS

Plenary/Invited Lectures

1974	Symp on High Resolution Spectroscopy (Columbus, Ohio)
1976	Symp on Molecular Structure (Austin, Texas)
1978	Faraday Society Spectroscopy Con (Bristol)
1979	14th Internat Free Radical Conf (Sanda, Japan)
	Symposium Interstellar Molecules (Meudon, France)
1980	University College Astronomy Symposium (London)
1981	Conference on Submillimetre Wave Astronomy (London)
	Advances in Spectroscopy, Faraday Meeting (London).
1983	British Association BAYS lecture (x2) (Sussex)
	Federation of Astronomical Socs, Herstmonceux
	RAS Disc Meeting on Interstellar Grains (London)
1984	Symposium on Molecular Structure (Austin, Texas)
	Microwave/IR Spectrosc of Transients (Cambridge)
	EUCHEM Reactive Species in Inorg Chem (Burghausen)
1985	High Resolution Spectroscopy Conference (York)
1986	NATO Workshop PAHs in Space (Les Houches)
	Conference on Molecular Astrophysics (Bruxelles)
	Symp on Planetary Science, Obs. de Paris (Meudon)
	Brioni Conference on Clusters (Brioni,Yugoslavia)
1987	Roy Soc Discussion on The Solar System (London)
	High Resolution Spectroscopy Symp (Dijon, France)
	Roy Soc of Chemistry Autumn Meeting (Nottingham)
	NASA Workshop on Carbon in Space (Ames CA)
1989	Internat Symp on New Aromatic Compounds (Osaka)
	Carbon Conference (Pennsylvania State)
	ACS Conference (Clusters) Miami
	Japan/UK SERC Symposium IMS (Okazaki, Japan)
	Faraday Discussion on Clusters (Warwick)
	6th ISNA Meeting (Osaka)
	Faraday meeting on Clusters (Warwick)
	19th Carbon Conference (Pennsylanvia State Univ)
1990	German Chem Soc Meeting, Organ Chem (Bad Nauheim)
	Solar System Workshop (Clemsen, North Carolina)
	IOP meeting (Warwick)
	Comet Meeting (Bad Honnef Bonn)
1991	4th Chemical Congress of North America (Fuel Science NY)
	6th Symposium on Macrocyclic Chemistry (Sheffield)
	20th Biennial Conference on Carbon (Santa Barbara)
	74th Canadian Chemistry Conference (McMaster, Hamilton)
	IOP Annual Meeting, Low Temperature Physics (Birmingham)
	Rank Prize Workshop on Molecular Cages (Lake District)
	British Association meeting BAYS lecture (Plymouth)
	Mackay Symposium (Birkbeck College)
	IAU Congress Astrochemistry (Campos de Jordao, Brazil)
	Swedish Physical Society (Stockholm)
	Fullerene Workshop (RISU, Roskilde, Denmark)
	Condensed Matter Physics 1991 (CMMP 91, Birmingham)
1992	Workshop on Atoms and Clusters 92 (Atami, Japan)
	Symp. on Atomic and Molecular Structure (Trentino)
	Portuguese Chemisty Society Meeting 1992 (Lisbon)

1st Italian Fullerene Conference (Bologna, Italy)
IOP meeting on Fullerenes (Rutherford Lab)
Universite Libre de Bruxelles Conference (Belgium)
Pittcon 92 Conference (New Orleans, USA)
American Physical Society meeting (Indianapolis)
Leermaker Symposium (Wesleyan U, Conn, USA)
Infrared Astronomy Conference (Calgary, Canada)
Adriatico Conference on Clusters (Trieste, Italy)
Invited Lecturer Cursos de Verano 92 (El Escorial)
European Materials Res Soc Meeting (Strasbourg)
IOP/RSC Joint Symposium on Fullerenes (London)
Vacuum Ultra Violet Meeting (VUV10, Paris)
11th Canadian Theoretical Chem. Conf. (Montreal)
12th Conf on Chemical Education (UCDavis, USA)
23rd European Conf, Mol Spectros (EUCMOS23, Vienna)
Symposium fur Theoretische Chemie (Blixen, Italy)
Gordon Conference on Clusters (Irsee, Germany)
Italgas Chemistry Prize Lecture (Turin)
University of Helsinki (Spec Lect) (Finland)
Gordon Combustion Conf (Spec Lect) (Hawaii)

1993 Italian Fullerene/Superconductivity Meeting - Pisa
Croatian Chemical Society Symposium - Zagreb
Fullerene/Superconductivity Meeting - Kirchberg
ACS Meeting (Fullerenes) - Denver
Sydney Leach Symposium - Paris
Theoretical Symposium - Namur
NATO Fullerene Workshop - Crete
Centenary Conf of Norwegian Chemical Society - Oslo
Fullerenes 93 Symposium - Santa Barbara
IURCAM Conference - Tokyo
Solid State Devices Conference - Tokyo
Span/American Inorg Chem Conf - Santiago (Spain)
Brioni International Conference - Brioni
Materials Conference - Wroclaw (x2)
Spanish Materials Conference - Oviedo
ACOLS Conference - Melbourne (x2)
London Schools Science Symposium

1994 Association of Science Education Conference (Birmingham)
New Organic Materials Conference (Madrid)
Science Research Institute Inaugural Meeting (Salford)
Student Chemical Society Centenary Meeting (Sheffield)
Berzelius Dagarna (Stockholm)
European Physical Society - Hewlett Packard Prize Lecture (Madrid)
Sussex University Science Teachers Conference (Sussex)
World Affairs Conference (Boulder, Colorado) (x2)
Cluster Workshop (Ameland, Netherlands) (x4)
3rd Workshop on Advances in Phys Chem (Nanjing, China)
Cursos de Verano Fullerene Workshop (El Escorial, Spain)
LVMH Science pour l'art Prize lecture (Paris, France)
Gordon Conference (Ceramic Materials) New Hampshire (special lecture)
Materials Research Soc Meeting (Boston)

Named/Special Lectureships

1992 Probst Lecture - Southern Illinois Univ (USA)

1993 Cherwell-Simon Lecture (Oxford)
Steinhofer Lecture (Kaiserslautern)

Dreyfus Lecture (UCLA)
John Coffin Memorial Lecture (University of London)
30th Anniv Lecturer (Chinese Univ of Hong Kong)

1994 Brode Lecturer (Whitman College, Washington, USA)
Winegard Lecturer (Guelph University, Ontario, Canada)
Kolthoff Lecturer (University of Minnesota, USA)
Rayleigh Lecturer (Harrow School
Chemical Inst of Canada Lecturer (Sherbrook University, Quebec, Canada)
Distinguished lecturer (University of Kentucky, Center for Applied Energy Research)

1995 Werner Lecturer (Trinity College, Dublin)
Tizard Lecturer (Westminster, School)

Research Seminars (Overseas)

1974 Bell Telephone Labs (NJ), NRC (Ottawa), UBC (Vancouver)
1976 Paris Sud (Orsay), Harvard, NRC (Ottawa)
1977 Lille, Brussels, Montreal, Waterloo
1978 Cal. State (L.A.), Cal Tech.(Pasadena), Arizona (Tucson), USC(Los Angeles), Herzberg Institute (NRC, Ottawa), UC Berkeley
1979 UBC (Vancouver), Montreal
1980 IBM (San Jose), UC Santa Barbara, USC (Los Angeles), Chemical Society Zurich
1981 UC Berkeley
1982 Trinity College (Dublin), NRC. (Ottawa)
1983 Basel, Kiel, Giessen, Inst.Rudger Boskovic (Zagreb)

1985 ETH (Zurich), Basel, Inst. R. Boskovic (Zagreb), Rice Univ. (Houston), Texas A&M, Texas Tech.

1986 Harvard, Guelph-Waterloo, Aachen (Tech Hochschule), Chicago

1987 USC (Los Angeles), UCLA (Astron), Berkeley, JPL (Pasadena)

1988 UCLA(Chem), Stanford, Arizona(Tucson), Arizona State (Tempe), Tech. Hochschul (Darmstadt), Max Planck Inst (Martinsried)

1989 MPI (Munich), UCLA(Chem), Oregon, JPL(Pasadena), Berkeley, NASA (Moffett Field), Toronto, Montreal, Guelph.

1991 California (Los Angeles, UCLA), California (Berkeley), Cal Tech (Pasadena), California (Santa Barbara, UCSB), Belo Horizonte (Brazil), Recife (Brazil), Erlangen, Freigburg, Heidelberg, Shell (Amsterdam), NIST (Washington) NRC (Ottawa), Arizona(Tucson)

1992 Pisa (Italy), Michigan (Ann Arbor, USA), Chicago (USA), McGill (Montreal, Canada), Chemical Society of Zurich, Laue Langevin Laboratory (Grenoble), Aarhus (Denmark), Helsinki (Finland), Niels Bohr Inst(Copenhagen), Stockholm (DHc lecture), Tokyo (Japan), Shinshu (Nagano, Japan), Kitagawa Industries (Tokyo Japan), Nobeyama Radio Observatory (Japan), NRC (Ottawa, Canada)

1993 Basel Chemical Society, ULB Bruxelles (DHC lecture), Josef Stefan Institute (Ljubljana), Limburg (DHC lectures), UC San Diego, Crete, NEC Japan, Shinshu, Shizuoka, Materials Institute (Warsaw), Milan, Berlin Chemical Society

1994 2xRSC (Belgium section) lectures (Brussels) (1 British School), Swedish Royal Academy (Stockholm), Stockholm University (Physics Dept), Herzberg Inst NRC Ottawa, Braunschweig, Scherring (Berlin), Humboldt Univ Berlin, Bielefeld, KFA (Julich), Peking U x2 (Beijing), Bell Labs NJ, UNAM Mexico City, UCLA (Astronomy)

1995

UK Research Seminars (* > 1)

Sussex (Chemistry, Physics, Astronomy, Biology*), Cambridge* (Chemistry and Astronomy Depts), Southampton*, Oxford*, Reading*, Nottingham*, Sheffield*, Warwick*, Glasgow, Strathclyde, East Anglia, Coleraine, Manchester*, Edinburgh*, Birmingham*, U.C. London* (Chemistry and Astronomy), Bristol*, ICI*, Surrey.

UK General Lectures for Students and Public (Chemistry/Astronomy)

Southampton*, Reading*, Sussex*, Exeter*, Bristol*, Bath, Surrey, Essex, Imperial College*, University College*, Cardiff*, Kent, Swansea, U.C.North Wales, Portsmouth, Leicester*, Loughborough, Thames, Durham, Leeds*, Nottingham*, Open University, Cambridge*, RSC (Sheffield) RSC (Cumberland), Brighton Astron. Soc.*, Eastbourne Astron.Soc., Croydon Astron. Soc., Alembic Club (Oxford), U.C. Sussex(Astron, Biology) Q.M.C*. Sussex Town and Gown, Mid-Kent Astronomy Society, Royal Institution (Friday Evening Discourse), East Midlands RSC.

1993	Bath, Cambridge, Imperial College, Birmingham, Warwick Royal Society, Nottingham, Liverpool, Pfizer Company,
1994	Leicester, Aston, Royal Institution (Friday Evening Discourse (#2)), Sussex, East Anglia, Surrey
1995	Durham, Liverpool, Queen's (Belfast), Coleraine

Schools'Lectures

Christ's Hospital School, Worthing Sixth Form College, Kingston Polytechnic (Schools Lecture), RSC Schools L RSC Essex Schools Lecture, Chelsea College, Charterhouse, London Schools (Q.M.C.), King's School Canterbury, St Dominics 6th form College Harrow, Dreyfus Schools' Lectures, 1986 at RoyalInstitution, St Paul's School for Girls Open Day Lectures (Sussex), Hurstpierpoint College BAYS Lecture(Southampton)

BROADCAST INTERVIEWS etc

1976	BBC Radio (Science Now) "Interstellar Chains"
1977	BBC Radio World Service "Interstellar Chains"
1979	BBC TV OU Film based on my lecture "Chemistry between the Stars"
1985	BBC Radio World Service "Chemistry in Space"
1985	BBC Radio Sussex "Chemistry in Space"
1986	BBC (Science Now) "C60,Buckminsterfullerene"
1989	USA Local Radio Carbon in Space)
1991	BBC Radio programme - "Science Now"
1992	BBC Radio World Service (x2)
1992	BBC TV "Molecules with Sunglasses" Horizon
1992	RAI TV Interview for Italian Television (Premio Italgas)
1992	NDR TV Nord Deutsche Rundfunk Programme on Fullerenes
1993	SFB Radio - Sender Freies Berlin, Radio
1993	UCLA video film Dreyfus Lecture
1994	BBC Select TV - Royal Institution Lecture

RESEARCH GRANTS

1970	Microwave Spectroscopy	(SRC)	10 000
1974	Microwave Spectroscopy	(SRC)	24 000

1974	Microwave Spectroscopy	(Sch)	10,000
1978	Photoelectron Spectroscopy (with M F Lappert)	(SRC)	18,000
1979	Computer	(SRC)	20,000
1977	PDF (with J F Nixon)	(SRC)	18,000
1977	Astronomy (with T Oka)	(NATO)	2,500
1981	Infra Red Spectroscopy	(SERC)	72,000
1980	Quad Mass Spectrometer	(RS)	5,000
1983	IR spectroscopy	(SERC)	20,000
1986	Jet Cooled i.r.spectroscopy	(SERC)	33,000
1987	Clusters (with A J Stace)	(SERC)	157,000
1992	Fullerene Chemistry with R Taylor/ D R M Walton	(BP/ICI/SERC)	200,000
1992	Cluster Rolling Grant with AJ Stace/J N Murrell)	(SERC)	300,000

MAIN RESEARCH COLLABORATION

The value of microwave and photoelectron techniques to a wide area of chemistry has been highlighted by fruitful collaboration with colleagues here at Sussex. One important research project carried out with D R M Walton involved the synthesis and study of long chain polyynes. This work led to our detection this species in interstellar space by Radioastronomy carried out with T Oka and astronomers at the Herzberg Institute for Astrophysics, NRCC Ottawa. A project, carried out with J F Nixon has opened up a new field of organophosphorus chemistry. Work has been carried out in collaboration with J P Maier (Basle) to study the ions of unstable molecules is now in progress. Cluster Beam studies on Carbon with R F Curl and R E Smalley (Rice). Astronomy Research has been carried out with M Jura at UCLA. The present Sussex Programme on Fullerene Chemistry is being carried out in collaboration with R Taylor and D R M Walton.

ASSOCIATED RESEARCH PERSONNEL

35 D.Phil students,
10 Chemistry by Thesis students
12 Postdoctoral Fellows.

POPULAR PRESS COVERAGE

Interstellar Molecule Discoveries,

Ottawa Citizen, The Times, The New York Times, New Scientist, Scientific American

Unstable Phoshorus Molecules:

New Scientist

Fullerenes

New York Times (x2), The Daily Telegraph, Houston Chronicle, New Scientist, C&E News, Omni, Sky and Telescope, Science Now, Economist, Der Spiegel, Time, Daily Telgraph.....

TEACHING EXPERIENCE

Lecture Courses (Sheffield University)

(1961-1963) taught O-level Chemistry at Sheffield Technical College

Lecture Courses (University of Sussex 1968-)

Chemistry Highlights Lectures for Freshers
1st and 2nd year Spectroscopy courses
Structural Methods (2nd year course)
Symmetry (2nd year)
Advanced Structure (3rd year course)
Valence Theory for Biochemists (2nd year course).
Rotational Spectroscopy (3rd year option)
Astrophysical Chemistry (3rd year option)
Topics in Chemical Physics (3rd year course)
High resolution Techniques (graduate course)

Lecture Courses (Univ. of Southern California, Los Angeles, 1981)

Chemistry & Spectroscopy of Interstellar Molecules

Seminars and Tutorials (Sussex)

Atomic and Molecular Structure (1st year course).
Mechanistic Principles (1st and 2nd year courses).
Thermodynamics (1 year course).
Conceptual Models (3rd year option course).
Synthesis (1st year course).
Statistical Mechanics

Practical Courses (Sussex)

1st year Introductory Practical Chemistry
2nd year Physical Chemistry (organiser 1978-80)
3rd year Chemistry and Chemical Physics Projects.

ADMINISTRATIVE POSITIONS

University of Sussex

Chairman of the University Safety Committee (1986-7)
School Undergraduate Admissions Organiser (1973-1976).
Chemistry by Thesis Sub-Board (1975-1978), Sec (1976-78).
Chemical Physics Subject Group, Secretary (1974-76), Chairman (1976-82 85-87).
Chemical Physics Sub-Board, Secretary (1974-76) Chairman (1979-83, 85-87)
School Joint Committee (1973-74, 77), Chairman (1974)
White House Careers Weekend (Weekend Residential Seminar Course on Careers for 3rd year students), Organiser (1974)
Editing, design and layout of "Chemistry at Sussex" School, Teaching and Research Handbook (copy available). The cover design was reproduced in "Modern Publicity", a major international annual of the best in graphic art and design
School Chemical Society Lecture Organiser (1987-)
University Senate (1979-1980).
Science Committee (1980, 1981-2, 1985-7)
Laboratory Director (1983-86): Overall responsibility for Tech Staff logistics, deployment, grading etc; School research strategy, budgeting, expenditure, building and laboratory space allocation.

C_{60}: Buckminsterfullerene

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School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Received May 2, 1991 (Revised Manuscript Received July 26, 199[illegible]

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Harry Kroto (left) was educated at Sheffield University and after periods at the National Research Council, Canada (1964–1966), and Bell Telephone Laboratories (1966–1967) went to the University of Sussex where he is now Professor of Chemistry. His research into the production and spectroscopic characterization of new species such as the phosphaalkenes, phosphaalkynes, thiocarbonyls, and polyynes led, via radioastronomy studies of interstellar molecules, to carbon cluster beam experiments aimed at understanding stellar chemistry. Wahab Allaf (right) who was educated at Aleppo University (Syria) and Sussex University is carrying out research on carbon clusters and laser chemistry. Simon Balm (center) who is studying cluster beam reactions and astrophysical chemistry was educated at Durham University and Sussex University.

I. Introduction

In 1967 Palmer and Shelef wrote the definitive review of the early work on carbon clusters in their article on the composition of carbon vapor.[1] Major advances have however been made in the interim period, and the overall situation has been updated by Weltner and Van Zee[2] who have given a very complete picture of the state of this fascinating field. Although Weltner and Van Zee's review is comprehensive (up to Nov 1, 1988), covering all aspects of carbon cluster properties, recent advances in the story of C_{60}, buckminsterfullerene (Figure 1) indicate that a specialized review is necessary and timely. The existence of the fullerenes as a family has now been established and it is useful to use a convenient nomenclature such as fullerene-60 or fullerene-70 which can apply to the whole family. There are of course numerous possible C_{60} and C_{70} cage isomers, however here we shall, in general, mean the most geodesically stable cages for which there is now no doubt in the case of the 60 and 70 atom species—they are (I_h)fullerene-60 and (D_{5h})fullerene-70 where standard symmetry labels have been added as prefixes. Since the existence of fullerene-60 and its spontaneous creation have ramifications in numerous areas from the properties of carbonaceous solids and microparticles through combustion, thermolysis, and synthetic organic chemistry to the nature of the carbonaceous constituents of space, these implications are also surveyed.

During a series of experiments in 1985 which probed the nature and chemical reactivity of the species produced during the nucleation of a carbon plasma the C_{60} species was discovered to be stable by Kroto, Heath, O'Brien, Curl, and Smalley.[3] It was proposed that this stability was due to geodesic and electronic properties inherent in the truncated icosahedral cage structure shown in Figure 1 and the molecule was named buckminsterfullerene. This novel proposal did not receive instant universal acceptance since it appeared to have been based on highly circumstantial evidence. Indeed it is now clear that there was a significant degree of scepticism in the minds of some with regard to the validity of the proposal, perhaps because the evidence was dispersed among many disparate scientific observations, much like the way that C_{60} itself may—we now realize—be involved in many processes involving carbon in the environment and space. However, systems giving rise to C_{60} were subjected to many detailed investigations subsequent to the discovery paper,[3] and some important points evolved which are worthy of highlighting:

(i) A wealth of convincing experimental evidence was amassed that showed that C_{60} possessed unique physicochemical stability—a conclusion totally independent of the cage structure proposal.

(ii) The fullerene cage proposal was the simplest and most elegant explanation of the unique behavior and no serious alternative explanation was ever presented.

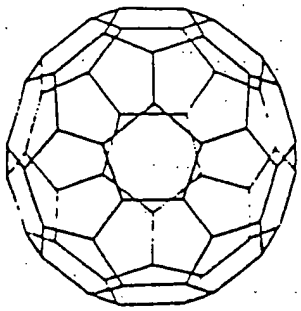

Figure 1. C_{60} buckminsterfullerene.

(iii) The proposal was consistent with many earlier observations on bulk carbon and clarified some previously unexplained phenomena in carbon chemistry.

The fullerene structural proposal has recently been confirmed by complementary observations from two groups. Kratschmer, Lamb, Fostiropoulos, and Huffman,[4] in following up their earlier IR investigation (in 1989)[5] which suggested that C_{60} might be present in arc-processed graphite, extracted a soluble material which formed crystals. The X-ray analysis showed the material to consist of 10-Å diameter spheroidal molecules and supplementary mass spectrometric and infrared data provided the first unequivocal evidence for C_{60} (and C_{70}). In a parallel, independent investigation which probed this same original key observation,[5] Taylor, Hare, Abdul-Sada, and Kroto[6] found that similarly arc-processed graphite gave rise to a 720 mass peak, commensurate with the presence of fullerene-60, and that this material was soluble and could be extracted directly. The extracted C_{60} compound yielded a single ^{13}C NMR line which proved that all 60 carbon atoms are equivalent as expected for the truncated icosahedral buckminsterfullerene structure. Taylor et al. also showed that C_{60} and C_{70} can be separated chromatographically and that the latter has the D_{5h} prolate, ellipsoidal structure first suggested by Heath et al.[6] These results provide further support for the conjecture that a whole family of fullerenes exists.[7,8]

Since these revelations, which are discussed further in section IX, the fullerene field has exploded and numerous groups are probing various facets of physicochemical properties of the fullerenes. Indeed a new field of carbon chemistry has been born, and the first faltering steps of the promising infant are described in section X. Thus this review is particularly timely as it is written at the precise moment when the final sentence in the last paragraph of the *first* chapter in the story of the fullerenes has been completed. The opening paragraphs in the next chapter are just being written and they herald a new era in which the flat world of polycyclic aromatic chemistry has been replaced by a postbuckminsterfullerene one in which round structures are favored under certain surprisingly common circumstances.[10] This article reviews the buckminsterfullerene story from the time when it was just a twinkle in the eyes of a few imaginative theoreticians, through the experiments which revealed that it actually formed spontaneously and exhibited stability to the most recent revelations that it could be isolated and did indeed possess the round hollow cage structure as proposed. As many contributions to the story as could be traced by Dec 1990 are included.

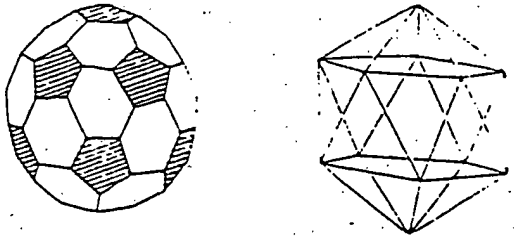

Figure 2. Diagram of C_{60} next to an icosahedron published in the book *Aromaticity* by Yoshida and Osawa.[14] These authors discuss (in Japanese) the "superaromaticity" which might accompany electron delocalization over a three dimensional truncated icosahedral pure carbon molecule.

II. Summary of Relevant Carbon Studies Prior to the Discovery of C_{60} Stability

At least part of the reason for the degree of interest engendered by the buckminsterfullerene proposal revolves around its high degree of symmetry. Mankind has always been fascinated by symmetric objects, indeed stone artifacts with the form of the Platonic solids, dating back to neolithic times, have been found in Scotland,[11] indicating that human beings have long had a spiritual affinity with abstract symmetry and an aesthetic fascination for symmetric objects. The truncated icosahedron is one of the Archimedian semiregular *solids*; however in *hollow* form an early example appears in the book *De Divina Proportione* by Fra Lucia Pacioli. A reproduction of this drawing by Leonardo Da Vinci entitled "VCOSEDRON ABSCISVS VACVVS" is to be found in the book *The Unknown Leonardo*,[12] which is rather more accessible than the original!

The C_{60} molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 1970[13] and discussed further in a chapter on "Superaromaticity" in a book by Yoshida and Osawa[14] in 1971; the original diagram is depicted in Figure 2. An equally imaginative article, which actually predates this work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages.[15,16] The next paper was that of Bochvar and Gal'pern in 1973 who also published a Hückel calculation on C_{60}.[17,18] In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for fullerene-60.[19] Davidson's orbital energy level diagram, depicted in Figure 3, was determined by using a calculator, and this paper contains an unusually prescient paragraph in the light of recent observations (particularly those in section VII): "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three-dimensional aromaticity." Haymet's study[20] on this molecule coincided very closely with its discovery in 1985.[3]

On the experimental front there were many very important early papers on carbon clusters and these have already been reviewed.[1,2] Perhaps the most interesting early carbon cluster papers (and the ones which in fact actually stimulated the discovery experiments) were

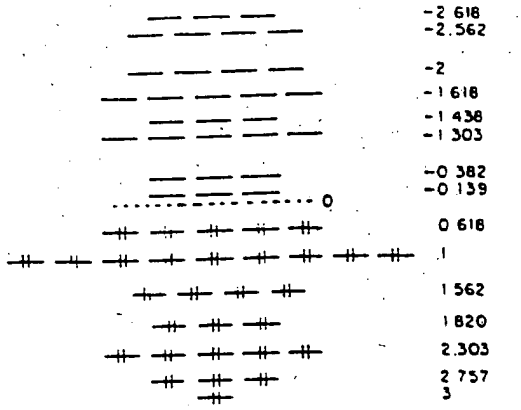

Figure 3. The Hückel molecular orbital calculation for buckminsterfullerene was carried out by Bochvar and Gal'pern[17,18] (1973) and Davidson[19] (1980), prior to, and by Haymet[20] (1985) coincidentally with, its discovery. The orbital energy level diagram (units of β) depicted here is that published by Davidson[19] who determined it using graph theory to obtain simplified algebraic relations which were evaluated with a calculator (reprinted from ref 19; copyright 1981 Springer-Verlag Publishers).

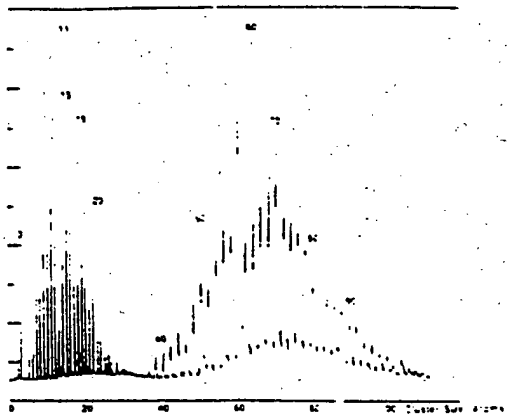

Figure 4. Time-of-flight mass spectrum observed by Rohlfing, Cox and Kaldor,[25] of carbon clusters produced by laser vaporization of graphite. In this experiment carbon clusters with $N = 1$–190 atoms were detected for the first time. These studies showed that only even-numbered clusters were stable (reprinted from ref 25, copyright 1984 the American Institute of Physics).

those published by Hintenberger and co-workers in 1959–63[21-24] in which it was shown that species with up to 33 carbon atoms could form in a carbon arc. The next important advance was made by Rohlfing, Cox, and Kaldor[25] in 1984 who found that much larger carbon clusters (C_n with n = 30–190) could be produced by vaporization of graphite (Figure 4). Rohlfing et al. used the supersonic nozzle, laser vaporization technique developed by Smalley and co-workers at Rice University[26] in 1981. In this technique clusters are made by laser vaporization of refractory materials into a pulse of helium or argon in the throat of a supersonic nozzle. The vaporized material nucleates in the gas pulse which then expands supersonically into a vacuum chamber where it cools and is skimmed. The skimmed beam passes into a second chamber where the entrained clusters are ionized by a second laser pulse and the cluster ion mass distributions determined by time of flight mass spectrometry (TOF-MS). The mass spectrum observed by Rohlfing et al.[25] is shown in Figure 4; they pointed out that only ions with *even* numbers of carbon atoms were observable for the new family of clusters with more than 30 carbon atoms. Packing or magic number effects are very weak under these conditions.[27] Bloomfield et al.[28] also studied carbon clusters by the same technique and observed both positive and negative *even* numbered ions. They also studied the fragmentation behavior of the new family and in particular chose the C_{60} cluster for further study and showed that it could be photodecomposed with 532-nm multiphoton laser radiation.

III. The Discovery of C_{60}: Buckminsterfullerene

In September 1985 the reactions of carbon clusters were investigated by the Rice/Sussex group.[2,29,30] These experiments were aimed at simulating the conditions under which carbon nucleates in the atmospheres of cool N-type red giant stars. Circumstantial evidence appeared to suggest[31,32] that such stars might be likely sources of the long carbon chain molecules in the interstellar medium and in particular that the formation process might be related in some important way to soot formation.[33] The interstellar cyanopolyynes (HC_nN (n = 5–11)) were discovered by a synergistic combination of laboratory microwave spectroscopy experiments,[33,34] theoretical analysis,[35] and observational radioastronomy.[36-39] The cluster beam experiments showed convincingly that species such as HC-N and HC_9N, which had been detected in space,[36-38] could be produced by such laboratory simulations of the conditions in carbon stars.[29,30] A second motivation for probing laser vaporization of graphite was the question of whether carbon clusters were associated with the so-called diffuse interstellar bands as Douglas had proposed in 1977.[40] The development of resonant 2-photon ionization in conjunction with the cluster beam technique to obtain the high-resolution spectrum of SiC_2 by Michalopoulos et al.[41] suggested that the electronic spectra of carbon clusters might be accessible by this technique. During the course of the experiments[29,30] which probed the behavior of the pure carbon clusters a striking discovery was made—under some clustering conditions the 720 mass peak appeared to be extremely strong (Figure 5).[3] Indeed the intensity of the C_{60} peak, relative to the adjacent cluster distribution, could be varied dramatically just by altering the conditions. In particular, conditions could be found for which the mass spectrum was totally dominated by the C_{60} peak—at least in the mass range accessible (Figure 6). It was concluded that C_{60} must be particularly stable to further nucleation and it was proposed that this might be explained by the geodesic factors inherent in a truncated icosahedral cage structure in which all the atoms were connected by sp^2 bonds and the remaining 60 π electrons distributed in such a way that aromatic character appeared highly likely.[3]

In these experiments it was found that the C_{70} peak also showed clear enhancement although to a lesser extent; the C_{60}/C_{70} ratio was ca. 5/1 in general. In previous experiments[25,27,28] the $C_{60}/(C_{58}$ or $C_{62})$ ratio was ca. 2/1 (Figure 4) whereas in the new experiments

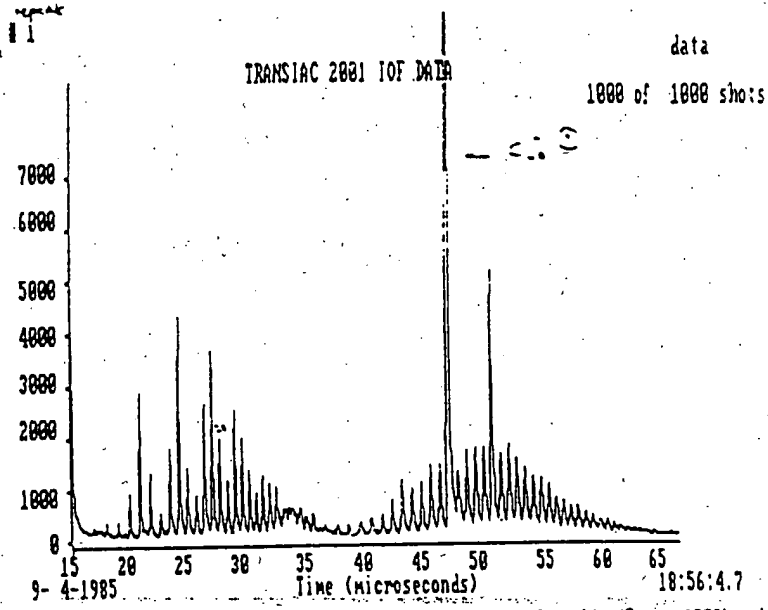

Figure 5. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite (Sept 4, 1985) under conditions which first exhibited the dominance of the C_{60} cluster and led to the recognition that 60 might be a "magic" number.

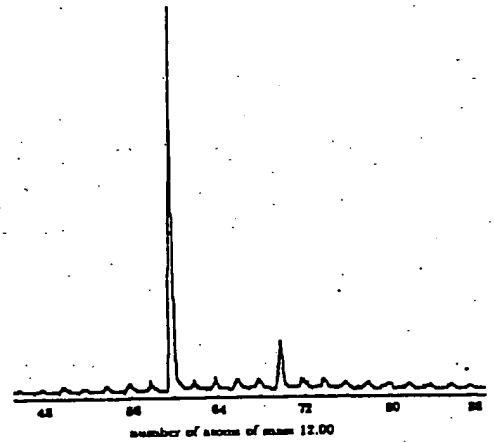

Figure 6. Time-of-flight mass spectrum carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant C_{60} cluster signal.[3] Note also the prominence of C_{70}.

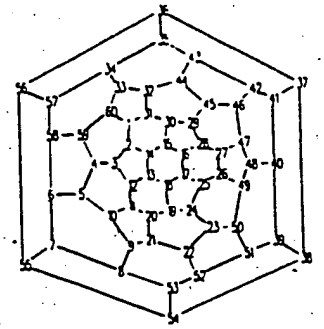

Figure 7. The IUPAC name of fullerene-60 determined by computer analysis—according to P. Rose.[47]

conditions were found in which a ratio of 20/1 or more was achieved (Figure 6). It was soon realized that although C_{60} generally appeared fairly special, the conditions under which it appeared dominant were rather unusual. They were conditions in which the major fraction of the carbon had nucleated to form macroscopic particles too large to be detectable by the mass spectrometer. Thus it was recognized that the signal shown in Figure 6 shows the "small" carbon species which remain when the microparticles have formed. Due to the fact that geodesic structural concepts were a guide to the hollow cage structural explanation that

cule was named after Buckminster Fuller, the inventor of the geodesic domes.[43] Although the name chosen, buckminsterfullerene[3,44] is a little long,[45,46] it is not as long as the IUPAC alternative and not as difficult to pronounce (Figure 7)[47] and certainly not as difficult to derive![48,49] The name fullerene can be conveniently and appositely used for the whole family of closed carbon cages with the 12 pentagons and N (other than one) hexagons in an sp^2 network.[8,44] For several reasons, not least the problem of ambiguity with international sports nomenclature, some other names are probably not as satisfactory; they are certainly less enlightening.

Since the buckminsterfullerene detection paper[3] was

work has been carried out. Two complementary accounts covering many of the important general implications and experimental observations have been given by Kroto[50] and Curl and Smalley.[51] More focused accounts have also been published dealing mainly with experimental observations,[52-54] astrophysical implications,[42,55-58] symmetry and structure considerations of fullerene-60, and the icosahedral giant fullerenes.[59-60] The chemical implications have also been discussed in Kroto[61] and Kroto and Walton.[10] Hirota[62] and Heath[63] discuss fullerene-60 as well as other novel carbon molecules.

IV. Sources of C_{60}

In the original work, which showed how conditions could be achieved to produce a signal in which the C_{60} peak was dominant, the pulsed nozzle/laser vaporization technique[26] was used to produce the clusters from a graphite target and photoionization TOF-MS used to detect them. The laser-produced plasma expanded into a high pressure (ca. 1–10 atm) of He and the target graphite surface was continually replenished so that the surface remained essentially flat. A nozzle extender was used to increase the clustering time prior to expansion to ca. 100 μs and the high He pressure increased the nucleation rate. Although initially it was conjectured that perhaps graphitic sheet fragments might have been ablated from the graphite target and rearranged into the buckminsterfullerene structure, subsequent considerations suggested that C_{60} was more likely to have formed by nucleation from carbon vapor consisting, at least initially, of C atoms and very small carbon molecules.[52] Negative ion distributions produced by crossing a laser with the cluster beam just as it exited the nozzle[64] have been studied, and the relationship between these and positive and negative ion distributions, obtained directly from the vaporization zone (i.e. without photoionization), has been discussed by Hahn et al.[65] and O'Brien et al.[66] The consensus of opinion was that C_{60} appeared to exhibit special behavior whether charged (positive or negative) or neutral and that the nucleation rate order was neutrals > cations > anions.[66] Very detailed discussion of the conditions under which C_{60} appears to be special has been given by Cox et al.[67] These studies are discussed in more detail in section V.

Carbon cluster distributions exhibiting dominant C_{60}^+ signals, can be produced in another way as O'Keefe, Rosa, and Baronavski[68] and Pradel et al.[69] have shown using high vacuum TOF-MS. In these experiments the graphite target is inside the mass spectrometer vacuum system and remains stationary. After several laser pulses a hole is drilled in the graphite and nucleation appears to occur in the cavity. McElvany et al.,[70] using ICR-MS techniques, have shown that if the axis of the laser-drilled hole is aligned parallel to the trapping magnetic field a strong C_{60}^+ signal predominates in the mass spectrum. In a study of the small cluster distribution, McElvany, Dunlap, and O'Keefe[71] found that the vaporization of a diamond target produces the same distribution as does graphite. This result indicates that the clusters appear to be produced by nucleation of atomic/molecular carbon vapor rather by a process involving the ablation of bulk fragments from the target. Meijer and Bethune[72] have modified the original laser vaporization procedure for producing C_{60}[3] in order to deposit material on a film. They have shown that the mass spectrum obtained by subsequent laser desorption of the resulting material yields a very similar cluster distribution to that of the cluster beam experiments. They have also carried out isotope scrambling measurements[73] supporting the conclusion that C_{60} is assembled from small carbon species in the gas phase after vaporization (see section VI).

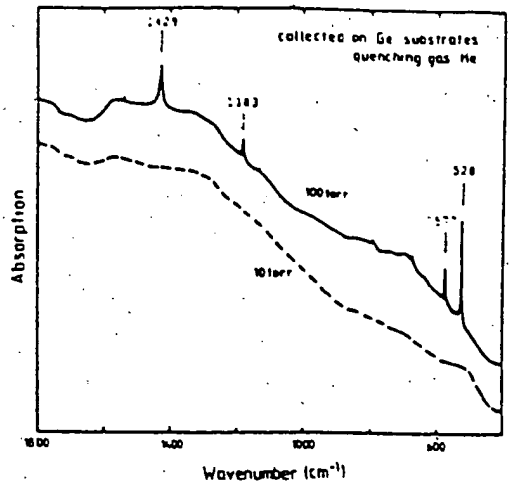

Figure 8. Infrared absorption spectrum observed in 1989 by Krätschmer, Fostiropoulos, and Huffman[3,74] from carbon produced by arc-discharge processing. Krätschmer et al. made the perceptive observation that the four sharp absorption features indicated might belong to fullerene-60. The frequencies were tantalizingly consistent with theoretical predictions (section VIII) for the fundamental vibrations of fullerene-60 (reprinted from ref 74; copyright 1990 Elsevier Science Publishers).

A fascinating and ultimately key observation was described in September 1989 by the Heidelberg/Tucson group: Krätschmer, Fostiropoulos, and Huffman[3,74] who detected four weak bands in the infrared spectrum of a film deposited from a carbon arc under argon (Figure 8). Krätschmer et al. pointed out that the vibrational frequencies of the four bands (and associated ^{13}C shifts) observed were in tantalizingly close agreement with theoretical estimates for fullerene-60 (details in sections VIII and IX).

Several other interesting studies have shown that laser vaporization of a wide variety of carbonaceous target materials (other than *pure* carbon) also yields a dominant C_{60} signal: e.g. carbon films (Creasy and Brenna[75]); polymers such as polyimides (Creasy and Brenna,[76] and Cambell et al.[77-79]), coal (Greenwood et al.[80]), polycyclic aromatic hydrocarbons (Giardini-Guidoni et al.,[81] and Lineman et al.[82,83]). Last but not least, So and Wilkins[84] have shown that C_{60} can be detected by laser desorption of soot! In fact they have observed even-numbered carbon clusters with as many as 600 carbon atoms (Figure 9). This result and similar experiments may indicate that giant fullerenes may also be forming.[80] All experiments show that conditions can be found in which the C_{60}^+ peak is either prominent or dominant. However conditions also exist for which this is not the case.[84] It is likely that the availability of many other pathways to "organic" (H-containing species) may be responsible for some of the latter observations.

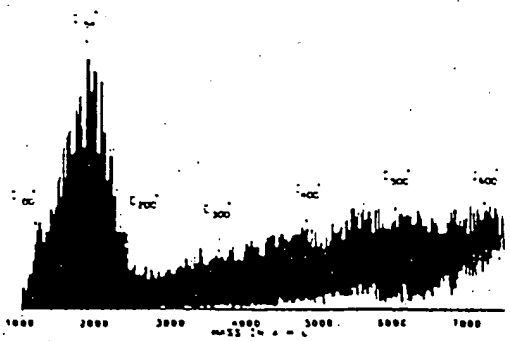

Figure 9. Laser desorption Fourier transform mass spectrum, observed by So and Wilkins,[84] of soot deposited on a KCl-coated stainless steel probe tip. Note that *all* the peaks here also correspond to *even* numbered carbon species. Since only even-numbered carbon aggregates can close perfectly it is possible that the explanation for this phenomenon is that these species are fullerenes and that the larger species are giant fullerenes of the kind depicted in Figure 22.

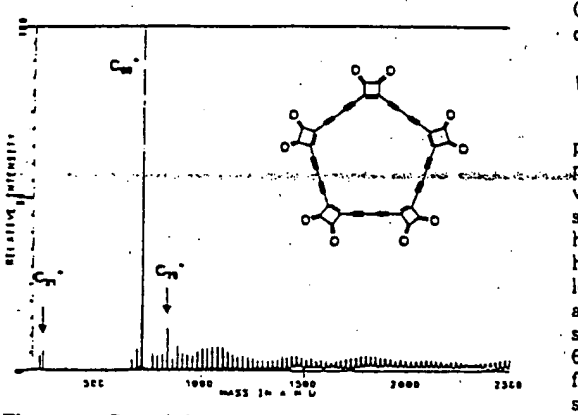

Figure 10. Remarkable positive-ion laser desorption Fourier transform mass spectrum, observed by Rubin et al.,[85] of the ring carbon oxide depicted under low laser power. This oxide which might be expected to decarbonylate to yield a C_{30} monocyclic ring has clearly dimersed to form C_{60} buckminsterfullerene!

A most exciting result was described by Rubin et al.[85] who have used a combination of organic synthesis and laser desorption mass spectrometry. In a preliminary study by the same group (Diederich et al.[86]) attempted to prepare pure carbon rings, a prominent peak for the C_{18} cluster was detected during mass spectrometric analysis of a laser desorbed 18-carbon ring precursor. This work has now been advanced in spectacular fashion; refined measurements on C_{18} and C_{24} precursors[85] yield mass spectra which show prominent C_{60} and C_{70} signals. However most striking is the observation that laser desorption of the C_{30} ring precursor produces a mass spectrum containing a totally dominant C_{60} signal! (Figure 10). This result suggests that, in the vapor phase, a spectacular dimerization process occurs in which two C_{30} polyyne/cumulene rings combine in a concerted folding rearrangement to form the C_{60} cage.[10] The implications of this process and indeed other aspects of the fullerene discovery for organic chemistry have been considered.[10,61]

Some of the most important of all these experiments were those of Homann and co-workers[87-90] who detected

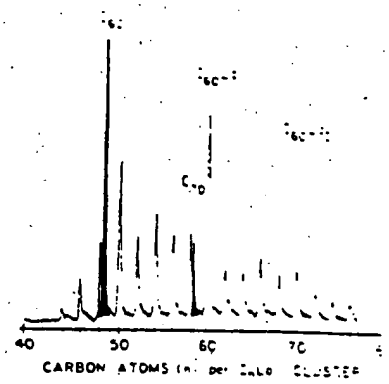

Figure 11. Mass spectrum of C_nLa cluster complexes and bare C_n clusters as observed by Heath et al.[7] when LaCl$_3$-doped graphite is laser vaporized (ArF 6.5 eV, 10 mJ cm^{-2}). Note the particularly strong peak for $C_{60}La$ and the absence of a peak for $C_{60}La_2$. This result is discussed in section VI (adapted from ref [7]).

C_{60}^+ in a sooting flame. These observations are discussed in more detail in section VII.

V. Stability and Intrinsic Properties of C_{60}

After the buckminsterfullerene structure was proposed[3] the intrinsic properties of the species were probed by the Rice/Sussex group.[50-54] It was clearly vital to determine how reliable the experimental observation of the "stability" of the C_{60} cluster was, i.e. how "special" or "magic" the cluster actually was and how certain one could be about the buckminsterfullerene hollow cage explanation. After all, the proposal appeared to rest entirely on the observation of a single, strong mass spectrum peak at 720 amu (Figures 5 and 6), and such highly circumstantial evidence needed further support. Mass spectrometry is particularly susceptible to erroneous conclusions drawn on the basis of magic numbers due to the likely presence of ionization and fragmentation artifacts. Various aspects of the original experiment led to the conclusion that the cation mass spectrum (Figures 5 and 6) was most probably an accurate reflection of the neutral cluster distribution. Nevertheless it was necessary to carry out experiments in order to probe the behavior of C_{60} more deeply in order to generate further evidence, albeit still circumstantial, to support the stability conclusion and the cage structure proposal.

During the period from 1985 to 1990 many experiments were performed by a number of groups operating in the cluster field which probed carbon behavior with a view to confirming or falsifying the fullerene-60 proposal. If C_{60} really were a cage then the most obvious next step was to attempt to trap an atom inside the cage. The first result, in this context, was the observation of $C_{60}La$ by Heath et al.[7] By using a graphite disk, soaked in $LaCl_3$ solution a strong signal was obtained for the monolanthanum complex $C_{60}La$, with no evidence of a peak for $C_{60}La_2$ (Figure 11). Cox et al.[91] questioned the conclusion. They pointed out that, since C_{60} needs two 6.4 eV (ArF) photons for ionization and $C_{60}La$ only one, the relative strengths of the $C_{60}La^+$ and bare C_{60}^+ MS signals should not necessarily be taken as reliable gauges of their respective abundances, and a possible $C_{60}La_n^+$ signal might be too weak to detect

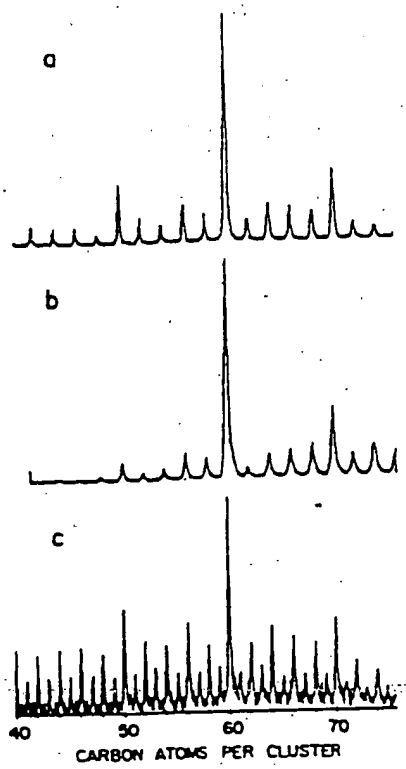

Figure 12. Carbon cluster ions observed under various production conditions:[62] (a) negative ions produced by directing a KrF excimer into the nozzle during expansion, (b) positive carbon cluster ions produced directly during vaporization in the nozzle without the aid of the KrF excimer laser, and (c) negative ions produced directly during vaporization in the nozzle, again without the aid of the KrF excimer laser but with longer residence time in the clustering region than in the case of the positive ions depicted in b (reprinted from ref 52; copyright 1987 Gordon and Breach Science Publishers, Inc.).

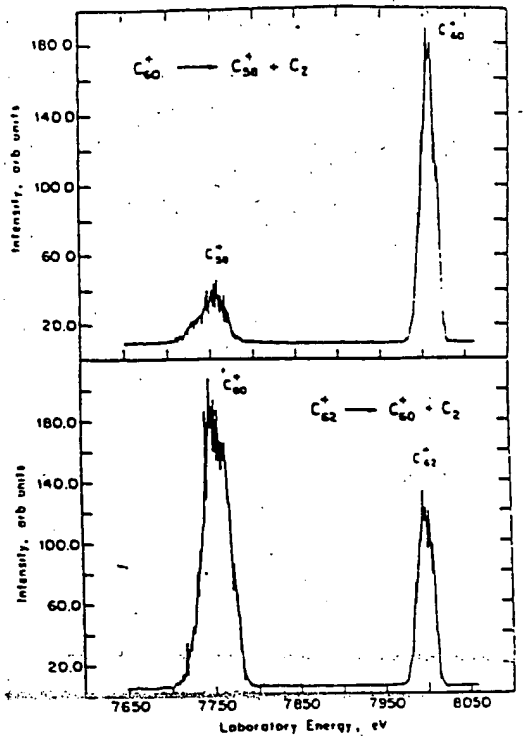

Figure 13. Metastable mass-analyzed ion kinetic energy scans (MIKES) published by Radi et al.[93] The parent ion (on the right) is mass selected by the magnetic analyzer and the horizontal axis is a scan of the electrostatic analyzer voltage. The parent ion energy is 8 keV. C_2 loss is observed from C_{60}^+ (above) and C_{62}^+ (below). Note the dramatic differences in metastable activity as reflected by the relative intensities of the product peaks, relative to their parent ions in these two cases (reprinted from ref 93; copyright 1990 the American Institute of Physics).

Cox et al.[67] have discussed further the cage hypothesis in general and metal atom encapsulation in particular and after detailed assessment they conclude that overall their observations are non-committal over whether C_{60} was a cage or not.

For the smaller carbon species the positive ions display the well known magic numbers: 11, 15, 19, 23 (the so-called "$\Delta n = 4$" effect, cf. Figure 4) whereas the negative ions exhibit a different sequence.[21-24,12] The paper announcing the original discovery[3] assumed that the mass spectra (Figures 5 and 6) reflected accurately neutral carbon cluster distributions. If the buckminsterfullerene structural proposal were correct however, the positive and negative ion distributions would be expected to exhibit a similar prominence for the 60-carbon atom analogue. The first experiment to probe this possibility[64] showed that negative ions, produced by laser ionization just after the cluster beam exited from the nozzle exhibited an anion mass spectrum in which C_{60}^- was dominant. In this experiment the neutral species became negatively charged by electron transfer. If the positive or negative ions, produced directly by vaporization are studied, it is found that only after clustering is allowed to continue for a significant length of time is the C_{60}^- anion dominant[66] otherwise it is not.[65] Some examples of mass spectra recorded under various conditions[51,64,65] are presented in Figure 12. Cox, Reichmann, and Kaldor[67] describe some intriguing relative time-of-flight differences in behavior between various individual clusters, in particular C_{28} and C_{60}, which are highly dependent on the nozzle parameters. These experiments appear to suggest that wall reactions may occur in the nucleation channel. It is possible that what was observed in this experiment was C_{60} deposited in the channel which subsequently desorbed. The main evidence for the importance of wall effects lies in the detection of $C_{60}K$ clusters when a new, pure (i.e. K free) carbon target replaces a previous one doped with potassium.

Important observations have had a bearing on the stability of C_{60}. The very early experiments by Bloomfield et al.[38] showed that C_{60} was susceptible to multiphoton fragmentation. A series of studies by Bowers and co-workers[92-94] showed that C_{60} could undergo metastable fragmentation. Particularly interesting is the observation that C_{60} exhibits much lower metastability than other neighboring clusters such as C_{58} as shown in Figure 13. These results suggest that hot C_{60} may exhibit phenomena associated with fluidity—perhaps an intriguing form of surface fluidity. On the

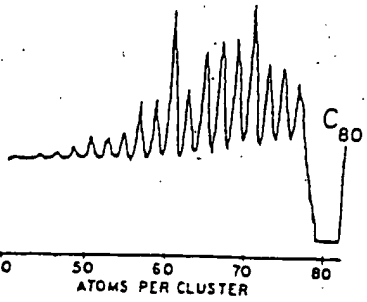

Figure 14. Fragmentation products under ArF (15 mJ cm^{-2}) irradiation observed by O'Brien et al.[95] Under irradiation the mass selected C_{80}^+ cluster (including ca. 20% C_{78} and ca. 10% C_{82}) is here seen to fragment into smaller even clusters: C_{76}, C_{74}, etc. by loss of C_2, C_4, etc. Particularly interesting is the observation that C_{60} and C_{70} are favored fragmentation products (reprinted from ref 95; copyright 1988 the American Institute of Physics).

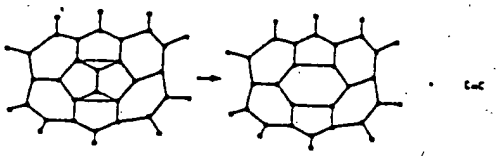

Figure 15. Hypothetical fragmentation–rearrangement mechanism presented by O'Brien et al.,[95] involving C_2 loss and cage re-sealing which could explain the fragmentation phenomena in Figure 14 (reprinted from ref 95; copyright 1988 the American Institute of Physics).

other hand, O'Brien et al.[95] and Weiss et al.[96] have shown that cold C_{60}^+ exhibits little, if any, evidence for fragmentation. The likely explanation for this disparity is that clusters produced under the vacuum vaporization conditions[23,92-94] possess massive amounts of internal energy leading to metastable C_{60}^+. As special behavior is most dramatic after extensive degrees of nucleation have occurred it is possible that the C_{60} signal observed under vacuum ablation conditions is actually a mixture of isomers, at least in part. Related studies by Hasselberger et al.[78] show that metastable fragmentation is less severe when clusters are produced with lower internal energies. The measurements of O'Brien et al.[95] showed that multiphoton fragmentation of clusters with 32–80 atoms occurred by elimination of even carbon fragments, C_n (n = 2, 4, 6, ...), rather than lower energy C_3 species. Particularly intriguing is the observation that large clusters, with 70 or more atoms fragment to form smaller even-cluster distributions in which C_{60} is special (Figure 14). Clusters with less than 32 atoms fragment into a range of smaller carbon species, a result interpreted as evidence that clusters with less than 32 atoms were not cages. O'Brien et al.[95] also presented an interesting mechanism for this process which is depicted in Figure 15. Laser irradiation studies by Weiss et al.[96] showed that the metal complexes were also quite resistant to photofragmentation. They also showed that multiphoton fragmentation of $C_{60}M^+$ resulted in metal-complex products C_nM^+ for which the critical smallest sizes occur at n = 48, 44, 44–42 for M = Cs, K, and La, respectively (Figure 16). This result provided strong circumstantial evidence for metal atom encapsulation because the minimum physical cage size scales with the ionic radius

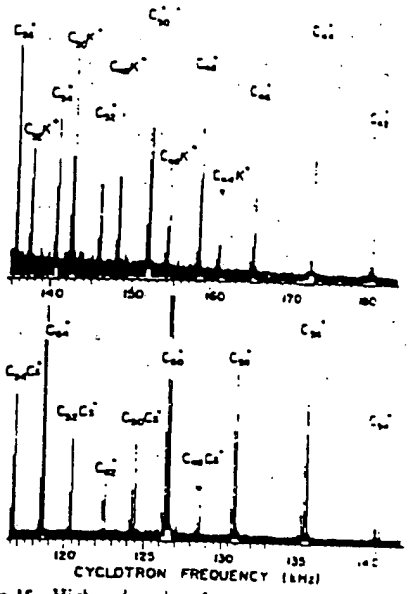

Figure 16. High-order photofragmentation pattern of $C_{60}K^+$ (above) and $C_{60}Cs^+$ (below) detected by FT-ICR mass spectrometry by Weiss et al.[96] The break-offs observed at $C_{46}Cs^+$ and $C_{44}K^+$ are in excellent agreement with expectation for the smallest fullerene networks capable of encapsulating the metals, based on the known ionic radii (reprinted from ref 96; copyright 1988 American Chemical Society).

of the metals in the series.

Prior to the isolation of macroscopic samples of the fullerenes (section IX) several experiments were carried out in order to determine their physical, mainly spectroscopic, properties. Tandem TOF-MS experiments were devised to explore the possibility that the spectra of C_{60} (neutral) and C_{60}^+ (the positive ion) might be responsible for the astrophysically intriguing diffuse interstellar bands (section XI). These experiments involved the resonant photodissociation of a van der Waals complex of benzene with neutral C_{60} and C_{60}^+. It proved possible to photofragment C_{60}-C_6H_6 but not the ion complex, C_{60}^+-C_6H_6, probably because charge transfer forces bind the adduct too tightly in the ion complex.[97] Very weak photofragmentation of the neutral complexes of C_{60} with C_6H_6 and CH_2Cl_2 was observed at 3860 Å by depletion spectroscopy.[98]

Yang et al.[99] used an ingenious technique developed by Cheshnovsky et al.[100] to observe the UV photoelectron spectra of negative cluster ions. In these experiments the spectra of carbon clusters from C_{48} to C_{84} have been observed. Of particular interest are the UPS patterns of C_{50}, C_{60}, and C_{70} which show a low energy LUMO feature consistent with closed shells for the neutral species. C_{60} had the lowest electron affinity: viz 2.6–2.8 eV. These observations provided further strong support for the fullerene proposal. The ionization potential of C_{60} was obtained in an elegant way by Zimmerman et al.[101,102] who used a series of charge transfer measurements with various reactants of known IP to bracket the IP of C_{60}: 7.61 ± 0.11 eV. This result was consistent with conclusions drawn from early experiments which indicated that the IP lay between the energy of the ArF excimer laser (6.4 eV) and that of the F_2 laser (7.9 eV) because C_{60} was 2-photon ionized by

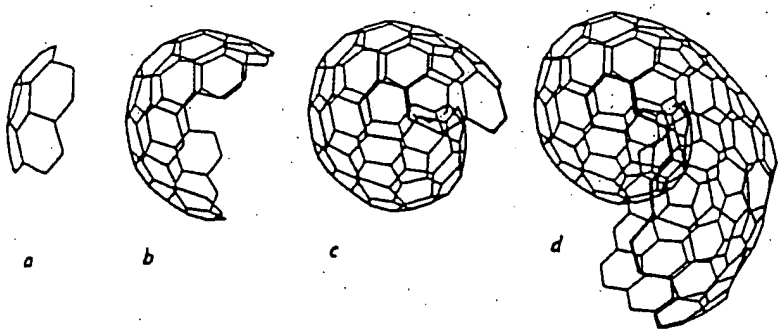

Figure 17. Diagramatic representation[108] of a hypothetical carbon vapor nucleation scheme[103,108] proposed for the formation of concentric shell graphite microparticles. Note that the structure c has overlapped and so trapped the trailing edge inside the spiraling network. This species is thus essentially the embryo for further growth. It is proposed that C_{60} might be produced by a modification of this process in which the edges meet and seal to form a closed cage. In such a case further growth by chemical bond formation might be expected to be halted. It was conjectured that similar structures might occur as intermediates during soot nucleation (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

ArF and 1-photon ionized by F_2.[103,67]

As mentioned in section IV, the most intriguing and convincing spectra were those obtained in the infrared study of Krätschmer, Fostiropoulos, and Huffman in 1990[5,74] (see further details in sections VIII and IX).

VI. Reaction Studies

The first reaction studies aimed at probing the cage concept were those of Heath et al.[7] and Cox et al.[91,67] (discussed in section V) who studied the carbon/metal complexes. Rohlfing et al.[25] and Heath et al.[29,30] carried out similar reaction studies which focused mainly on the properties of the carbon chains. It is also important to note that van der Waals complexes can form in the supersonic beam if C_{60} is cold.

When various gases such as CO, NO, and SO_2 were introduced into a reactor, placed downstream from the nozzle in which C_{60} is formed, Zhang et al.[103] showed that all the even carbon clusters were totally unreactive. The odd clusters were, on the other hand, very reactive. These experiments gained significant further support from the studies of McElvany et al.[70] and Weiss et al.[96] which showed C_{60} and its analogues to be extremely unreactive in an ICR trap. However if gases are mixed with the driver gas in the nozzle, reactions can take place before and after C_{60} is formed. With hydrogen, a wide range of hydrocarbon products is detected (Rohlfing,[104] Hallett et al.,[105] and Doverstal et al.[106]). Rohlfing has used an in-line reflectron modification of the cluster beam technique and made some very careful high-resolution mass spectrometric measurements of the reactions of clusters C_{20}–C_{80} with hydrogen.[104] The variations in reactivity appear to be structure related and consistent with the cage proposal. The study suggests that chain cluster species with as many as 44 carbon atoms may be present. Complementary experiments by Hallett et al.[105] and Doverstal et al.[106] indicate that clusters in the C_{20}–C_{40} range show at least three different types of reactivity as evidenced by the mass spectrometric patterns of the hydrogenated products. The observations[105] are consistent with the proposal that small fullerenes (C_{20}, C_{24}, C_{28}, C_{32}, C_{60}) can form.[8] They are also consistent with the fact that formation that no 22 atom fullerene can exist, as pointed out by Fowler and Steer.[107]

VII. Gas-Phase Carbon Nucleation and C_{60} Formation

It would appear that most workers in the field are able to observe special behavior fairly easily and under a wide range of conditions, all of which have one major feature in common: C_{60} appears to be dominant *only* when nucleation nears completion, leaving behind C_{60} and other even-numbered relatives such as C_{70}. This result has one obviously simple explanation; at least some fraction of the even clusters—particularly C_{60}—is unreactive toward growth into macroscopic particles. The spontaneous creation of C_{60} requires a mechanistic explanation. In particular, entropy factors clearly need to be carefully assessed when it is proposed that so symmetric an object is formed in a chaotic plasma. A feasible nucleation mechanism was provided by Zhang et al.[103] and refined further by Kroto and McKay.[108] The nucleation model proposes that curved sp^2-linked (aromatic) carbon networks form (Figure 17) and can serve as embryos for further growth. The energetics of sheet carbon cluster radicals is invoked to explain the curvature/partial closure. Essentially the drive toward closure is governed by the energy released as a result of eliminating the edge dangling bonds. For instance a flat graphite-like sheet of 60 atoms would have at least 20 dangling bonds, whereas fullerene-60 would, of course, have none. In general, in a chaotic system, partly closed, overlapped embryos, such as that shown in Figure 16c, are expected to form and which, once overlapped, cannot close perfectly. These species are probably highly active nucleation sites to which permanent chemical binding of adsorbing fragments can take place. Of course some form of closure/annealing process might take place if the temperature is high enough for intra and extra network rearrangement to occur. It was proposed[103,108] that during this general spiral nucleation process some embryos would close forming fullerenes, particularly fullerene-60 which would no longer present a site for efficient accretion. The process is primarily a physicochemical nucleation scheme in which the fullerenes act as deadends for the most rapid nucleation.

After embryo formation, epitaxial growth has been shown to result in icospiral graphitic giant molecules or microparticles[108] with structures consistent with

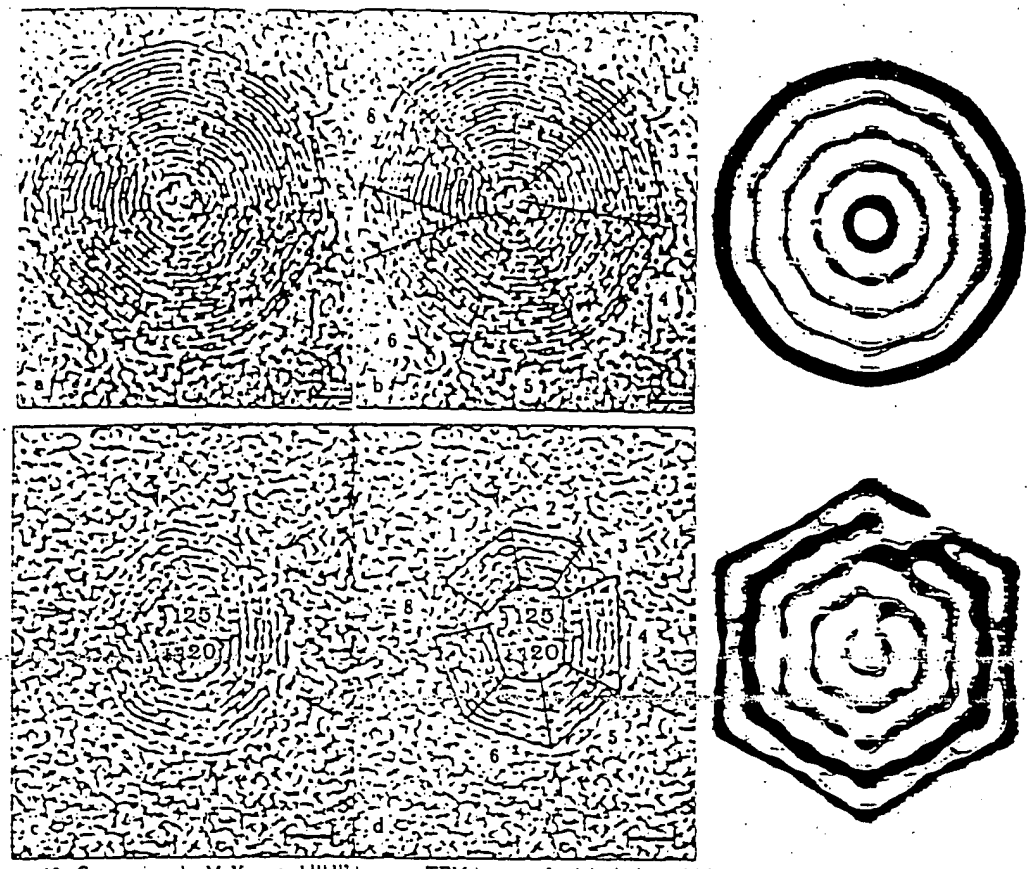

Figure 18. Comparison by McKay et al.[111,112] between TEM images of polyhedral graphitic microparticles observed by Iijima[108] and simulated TEM images for a hypothetical spiral shell particle predicted by the nucleation scheme depicted in Figure 17. The fairly round particle observed by Iijima which is depicted in a and b is seen to exhibit a similar pattern to the simulation top right. On the other hand the more polygonal particle, shown in c and d, exhibits a similar pattern to the simulation shown bottom right. The simulations are for the same particle observed from different angles. The hypothetical particle has shell interconnections which can most easily be seen in the lower right simulation. In b and d the polygonal outlines are delineated.

those of spheroidal graphitic microparticles observed by Iijima in 1980.[109,110] Kroto et al.[111,112] have provided further support for the scheme in the form of TEM image simulations based on the icospiral concentric shell structure concept,[108] in excellent agreement with the Iijima images as depicted in Figure 18. Roulston et al.[113] have shown that certain electronic and structural properties of amorphous semiconducting carbons can be explained on the basis of a spheroidal graphitic infrastructure, rather than by the traditional flat microstructure. Yacaman et al.[114,115] have shown that FT power-spectra processed, electron microscope images of carbon microparticles appear to be consistent with the quasiicosahedral spiral substructure.[108] Attention has been drawn to the fact that small graphitic microparticles actually consist of crystalline quasiicosahedral graphitic cores surrounded by amorphous carbon surface layers.[116,109] Interestingly, Iijima[110] has shown that the TEM structure at the nucleus of one of the carbon microparticles, studied earlier[108] was consistent with the image expected if it were a C_{60} cage. With hindsight this result demands further serious investigation to see whether fullerene-60 can itself be encapsulated during later stages of particle growth.

Wales[117] has considered some statistical aspects of the growth dynamics of closed-cage structures and Bernholc and Phillips have discussed the kinetic factors involved in the growth of carbon clusters in general.[118]

It was also suggested that a modified form of the nucleation scheme, devised to account for the spontaneous creation of C_{60}, could also explain the spheroidal nature of soot.[103,108,50,51,119] This proposal was criticized by Frenklach, Ebert, and co-workers[120-123] who favor an earlier theory, which invokes the physical condensation of flat PAH molecules held together by van der Waals forces into coagulating liquid drops. However, Harris and Weiner point out how little has been firmly established about the soot formation mechanism.[124] It can in fact be demonstrated[125] that the new scheme is broadly consistent with kinetic, structural, and chemical observations made on soot and its formation process.

The new nucleation scheme predicts that some C_{60} should form as a byproduct[103,108] of soot production. Subsequently Gerhardt, Löffler and Homann,[87-90] in studies of the ions produced in a sooting flame, found conditions under which the mass spectrum shown in

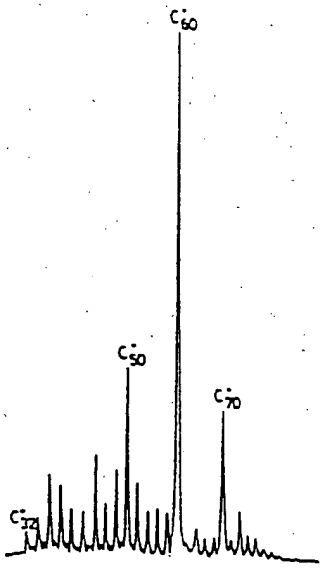

Figure 19. Mass spectrum, observed by Gerhardt, Löffler, and Homann,[87-90] of positive ions produced by a sooting benzene-oxygen flame (C/O = 0.76) (reprinted from ref 87; copyright 1987 Elsevier Science Publishers).

Figure 19 is obtained. This spectrum is almost identical with that observed during the pure carbon laser vaporization experiments where C_{60}^+ is the dominant ion! Homann and co-workers conclude that this observation should not be taken as support for the new spiral nucleation scenario as the tell-tale even ions with a dominant C_{60}^+ peak are not seen until after the inception of soot particle formation. The carbon/hydrogen reaction studies[104-106] promise to shed further light on the soot formation process, but the way in which the results might dovetail with the conventional data remains to be ascertained. Kroto has summarized the present state of affairs from this viewpoint.[125]

VIII. Theoretical Studies of the Fullerenes

Theoretical studies predating the discovery of C_{60} have been discussed in section II. After the discovery, theoreticians had a ball and many aspects of the molecule's properties have already been probed. The comprehensive overview of theoretical work on fullerene-60 presented by Weltner and Van Zee[2] is here conflated with more recent work.

One important aspect of the original experimental observations was the fact that C_{70} *also* showed special behavior. Topological and chemical stability arguments, as discussed by Kroto[6] and Schmalz et al.,[7] explain this observation as being entirely consistent with the fullerene proposal. Indeed these studies suggested that if the C_{60} mass spectrometric signal were due to its having a closed cage fullerene structure, C_{70} should show special behavior also, for the same reason. Thus most importantly and rather convincingly, the fullerene structure proposal no longer rested on the single line observation. In fact it had now gained significant further support by the fact that a prediction had been made and neatly confirmed. Indeed the two observations, taken together, provided convincing evidence for the existence of a whole family of fullerenes and further probing suggested that in addition to C_{60} and C_{70}, the C_{24}, C_{28}, C_{32}, and C_{50} clusters (Figure 20) should also show varying degrees of special stability[8,9] (N.B. fullerene-22 cannot exist[107]).

The dominance of C_{60} and C_{70} was ascribed to the fact that these are the smallest fullerenes that can have an isomer (one in each case) in which none of the 12 pentagonal configurations, necessary and sufficient for closure, abut.[8,9] It was shown[8,50] that the predictions were commensurate with the mass spectrum obtained by Cox et al.[67] (Figure 21) and consequently there existed convincing experimental evidence for the fullerene *family* proposal. Since even-numbered carbon clusters are detectable with as many as 600 or more carbon atoms,[84] the possibility of giant fullerenes[102,125] such as C_{240} and C_{540} shown in Figure 22 appears to be an exciting possibility.[60]

Isomer stability has been discussed by Stone and Wales[127] who noted that the difference in energy between isomers is small and suggested that the C_{60} signal should be due to a mixture of isomers. This result is difficult to reconcile with the observation (Figures 5 and 6) since it leads to the conclusion that C_{60} is no more special than other clusters such as C_{62}. Potential energy functions have now been developed for the carbon cages systems by Takai et al.[128] and Balm et al.[129] The simulated annealing, Monte-Carlo methods used by Zerbetto[130] to study the behavior of small carbon clusters have been applied by Ballone and Milani[131] in order to show that the fullerene cages are minimum energy structures.

A group theoretical analysis of the electronic properties of the fullerene family, by Fowler and Steer,[107] showed that the members, C_n where $n = 60 + 6k$ (k = 0, 2, 3, 4, ..., i.e. an integer other than one), should have closed-shell electronic structures. The degree of aromaticity in a compound is of interest, and the number of Kekulé structures is often considered to be a guide. A total of 12 500 for fullerene-60 has been calculated

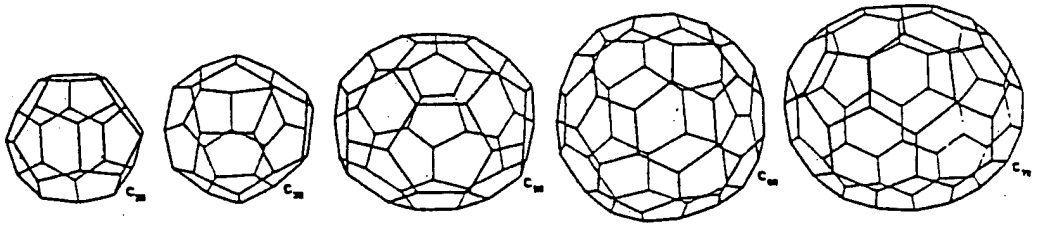

Figure 20. Five possible "magic" fullerenes predicted to display enhanced stability, relative to others in the range with 20–80 atoms, on the basis of chemical and geodesic factors[8] (reprinted from ref 8; copyright 1987 Macmillan Magazines Ltd.).

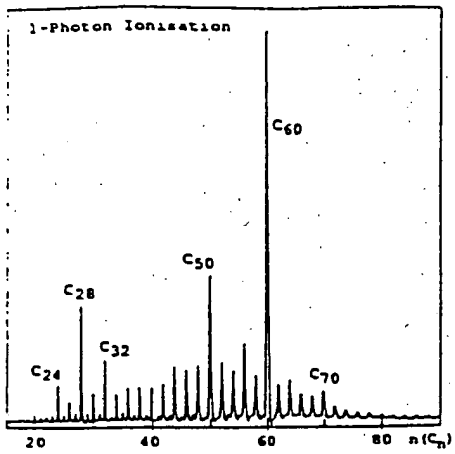

Figure 21. Time-of-flight mass spectrum taken from the data of Cox, Reichmann, and Kaldor.[67] The strong peaks are in excellent agreement with expectation[8,9] if they correspond to fullerenes. The fullerenes 24, 28, 32, 50, 60, and 70 (Figure 20) are predicted to exhibit enhanced stability, i.e. are magic. Note the sharp cutoff at C_{24} which is consistent with the fact that a no 22 atom fullerene can form.

by Schmalz et al.,[132] Hosoya,[133] Brendsdal and Cyvin,[134] and by Elser.[135] Resonance circuit theory has been applied to this problem by Schmalz et al.,[132,9] Klein et al.,[136,137] as well as Randic, Nikolic, and Trinajstic.[138–140] These studies indicate that account must be taken of the fact that some resonance structures make negative contributions to the aromatic stabilization. Schmalz et al.[9] compared resonance circuit theory with Hückel molecular orbital (HMO) theory and concluded that C_{60} should be less aromatic than benzene. Amic and Trinajstic[140] discuss stabilization arising from bond delocalization. Graph theory has been applied to C_{60} and to other systems by Balasubramanian and Liu[141,142] and also by Dias who has circumvented group theory in order to simplify Hückel calculations.[143] Hückel calculations on fullerene-60 have been made by Haymet[144,20] and the stabilization due to delocalization discussed. Jiang and Zhang[145] have calculated the stability of fullerene-60 by Hückel theory using moment analysis techniques. Hess and Schaad[146] as well as Aihara and Hosoya[147] have also applied Hückel theory to the problem, focusing on aspects of spheroidal aromaticity.

Fowler and Woolrich[148] have made three-dimensional HMO calculations which predict that C_{60} and C_{70} are closed shell systems. Fowler[149] extended this approach in order to assess the stability in other, larger fullerene cages, while Fowler, Cremona, and Steer[150] have discussed bonding in nonicosahedral spheroidal fullerene cages. Fowler[151] has extended these ideas to various classes of cylindrical fullerenes and predicted closed electronic shells with an empty nonbonding orbital for clusters consisting of $10(7 + 3k)$ and $12(7 + 3k)$ atoms with 5- and 6-fold symmetry. Ceulemans and Fowler[152,153] considered possible Jahn–Teller distortion pathways for icosahedral molecules.

Byers Brown[154] has discussed the simplification that high symmetry imparts to π-system calculations and obtained algebraic solutions for the orbital energies of fullerene-60. Electronic and vibrational properties were calculated by using a two-dimensional HMO method by Coulombeau and Rassat.[155] Semiempirical calculations including the effects of nonplanar π-orbital overlap due to curvature have also been carried out by using the free-electron model in the Coulson–Golubiewski, self-consistent Hückel approximation by Ozaki and Takahashi.[156] Haddon et al.[157,158] have also considered the effects of nonplanarity, i.e. pyramidalization.

Extended Hückel calculations by Bochvar, Gal'pern, and Stankevich[159] and INDO and INDO/CI calculations by Feng et al.[160] have been applied to C_{60} and its isomers. A comparison between C_{60} and graphite was made by MNDO with geometry optimization by Newton and Stanton.[161] McKee and Herndon[162] also applied MNDO theory to cage carbons and concluded that the flat "graphitene" cage,[144] in which two coronene sheets are linked by pentagonal rings at the edge to form a disk-like structure should be more stable than fullerene-60. These authors also considered the mechanism of formation arising from rearrangement. Rehybridization and bonding were studied by Haddon, Brus, and Raghavachari who applied the π-orbital axis vector/3d-HMO (POAV/3D HMO) method[157,158] and concluded that larger clusters were favored. It was also postulated that fullerene-240 should be more stable than C_{60}. Lüthi and Almlöf[163–165] have carried out

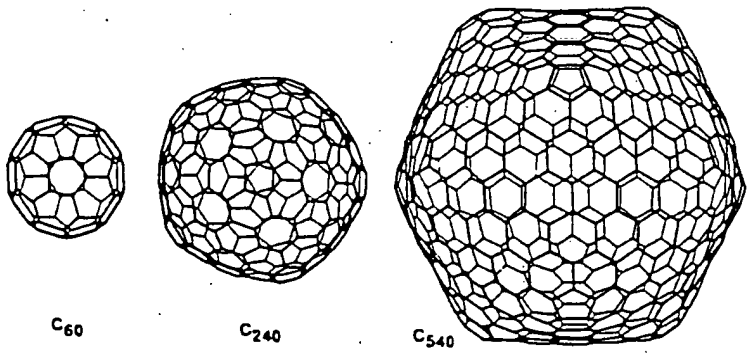

Figure 22. The set of fullerenes C_{60}, C_{240}, and C_{540} with diameters in the ratio 1:2:3. Kroto and McKay[108] showed that quasiicosahedral shape develops rapidly for the giant fullerenes. Strain in the giant fullerenes is expected to be focused in the regions of the corannulene-like cusps. The surface thus becomes a smoothly curving network connecting the twelve cusps (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

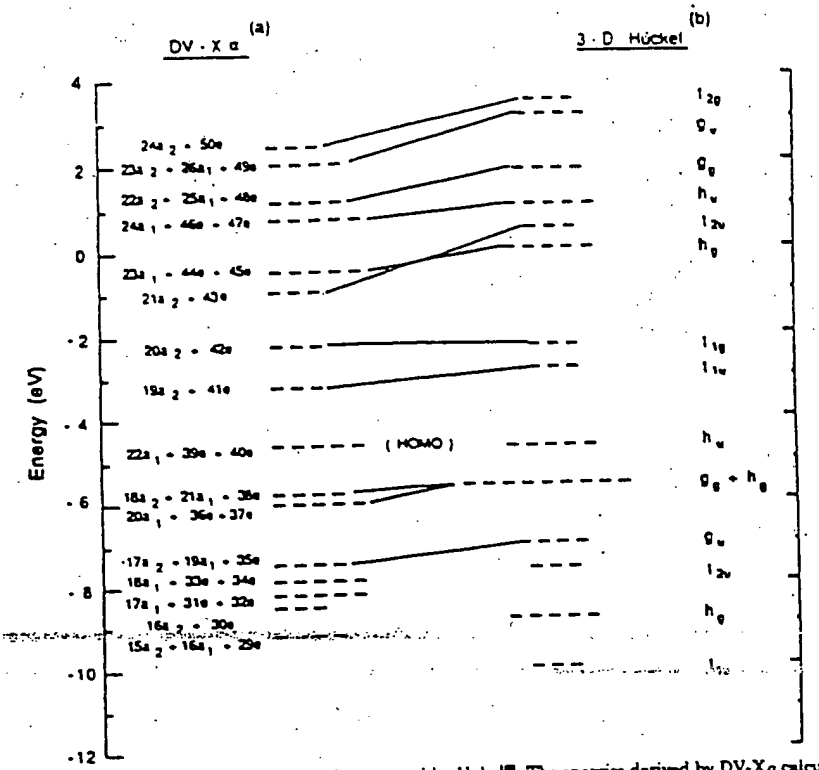

Figure 23. Orbital energy level diagram for fullerene-60 presented by Hale.[169] The energies derived by DV-Xα calculations assuming D_2 symmetry on the left are compared with Hückel results. In the diagram β has been given the value -2.52 eV (reprinted from ref 169; copyright 1986 American Chemical Society).

large-scale restricted Hartree-Fock calculations and they deduced that ΔH_f = 415–490 kcal/mol (relative to graphite) the electron affinity should be 0.8 eV and the ionization energy 7.92 eV. The electron affinity (2.4 eV) has been calculated by Larsson, Volosov, and Rosen[166] and by Braga et al.[167] Schulman and Disch[168] have calculated the heat of formation on the basis of ab initio SCF theory.

Hale[169] determined electronic properties, such as the ionization energy for fullerene-60, by the discrete variational (DV)-Xα method using the Slater transition state formalism. Such calculations tend to be good for spheroidal systems. Hale's orbital energy level diagram for fullerene-60 is reproduced in Figure 23. The linear combination of muffin-tin orbital method in its atomic sphere approximation (LMTO ASA) was applied by Satpathy.[170] Calculations in which the partial retention of differential overlap PRDDO approach was applied were carried out by Marynick and Estreicher.[171] Stone's tensor surface harmonic theory was used by Fowler and Woolrich.[148] The IMOA method (iterative maximum overlap approximation) was applied to a range of fullerenes by Kovacević, Graovac, and Babić[172] to assess hybridization, structure and the amount of strain in these cages. Haddon[173] has discussed degree of pyramidalization considerations for fullerene-60 and other aromatic compounds.

Fabre and Rassat have reviewed the properties of known aromatic molecules which are essentially com-

In some of the calculations the electronic spectra of the fullerenes were the main focus. The calculations of Kataoka and Nakajima[175] and László and Udvardi[176] used the Pariser–Parr–Pople method (with CI) to determine spectra, structural parameters, and oscillator strengths. Optimized INDO calculations were published by Shibuya and Yoshitani.[177] The electronic structure and the spectra have also been studied by the CNDO/S method (including CI) by Larsson et al.[166] and by Braga et al.[167] Hayden and Mele[178] evaluated π-bonding behavior using the tight-binding model with electron–phonon coupling for the ground and excited states of fullerene-60. Jahn–Teller instabilities in the excited electronic states and the ion have been classified by Negri, Orlandi, and Zerbetto[179] who have also estimated Franck–Condon patterns and phosphorescence quantum yields.

Several calculations focused on the vibrational properties of fullerene-60. The result of primary (and historical) significance is that only four fundamentals are IR active due to the high symmetry of the molecule. Of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, four have t_{1u} symmetry and are IR active whereas 10 (eight h_g and two a_g) are Raman active.

Newton and Stanton[161] gave preliminary details of the vibrational behavior of fullerene-60 using MNDO theory. A non-Cartesian coordinate method was employed to describe the C_{60} vibrations in terms of four-force field constants by Weeks, Jalabi, and Cooper.[180] Ab initio

SCF/STO-3G calculations of the vibrational properties of C_{60} and other symmetric carbon cages have been published by Disch and Schulman.[181] Schulman et al.[182] have applied the ab initio and AM1 methods to fullerene-24 and fullerene-60 in order to obtain heats of formation, vibrational frequencies, and ionization energies. Coulombeau and Rassat have considered the vibrations of several fullerenes up to fullerene-120.[183] They have also discussed hydrofullerenes.[184] In addition to calculating the rotational properties on the basis of icosahedral symmetry analysis,[184] Weeks and Harter have carried out a normal mode study on the basis of a classical spring/mass model.[185] They have also discussed the rovibrational properties of fullerene-60.[185-189] Stanton and Newton[190] extended and revised earlier MNDO studies giving detailed information on the normal modes. They have derived group theory invariance theorems for vibrational analysis and have discussed the A_u vibration which essentially consists of rotary oscillations of the pentagonal rings. Cyvin et al.[191] used a 5-parameter force field to calculate the frequencies of the four IR active and 10 Raman-active modes; and Brendsdal et al.[192] have considered approximate methods in order to determine all 46 vibrational frequencies. Brendsdal[193] has discussed the symmetry coordinates.

Slanina et al. have carried out a harmonic vibrational analysis within the AM1 method for fullerene-60 and also fullerene-70.[194] The study has been extended to include consideration of structural, energetic, and thermodynamic properties of both species using MMP2 and MNDO methods.[195-197] Bakowies and Thiel[198,199] have used the MNDO approach to calculate the IR spectra of a whole range of fullerenes from C_{24}–C_{240}. For C_{70} they deduce that one vibrational band should be significantly more intense than the rest, see section X.

Heymann has discussed the possibility that He may be trapped in a fullerene-60 cage.[200] Calculations have been made of the spectroscopic properties of various intracage complexes by Ballester et al.[201] assuming the central atom is trapped in a polarizable uniform (spherical) dielectric cage. Kroto and Jura[202] have discussed the importance of charge-transfer processes in the spectra of neutral and ionic fullerene intra- as well as extracage (van der Waals) complexes. For the ions the energy is just the difference between the ionization potentials of the C_{60} cage and the encapsulated species. Van der Waals complexes such as C_{60}·H^+ are likely to be particularly important (section XI). Rosen and Waestberg have calculated the electronic structure of $C_{60}La$ (and C_{60}) obtaining ionization energies and electron affinities for the neutral and ionic species within the local-density approximation.[203,204] Saito[205] has also used the local density approximation to calculate the electronic properties of $C_{60}M$ (M = K, O, Cl).

Theoretical calculations have been carried out on fullerene-60 derivatives such as hydrofullerenes by Coulombeau and Rassat[184] and by Scuseria[206] who has also considered the perfluorofullerene, $C_{60}F_{60}$. Crystal packing considerations for spheroidal molecules including fullerene-60, have been discussed by Williams.[207]

Several papers have focused on the likely electrical and/or magnetic properties of the fullerenes in particular fullerene-60. Elser and Haddon[208,209] using HMO

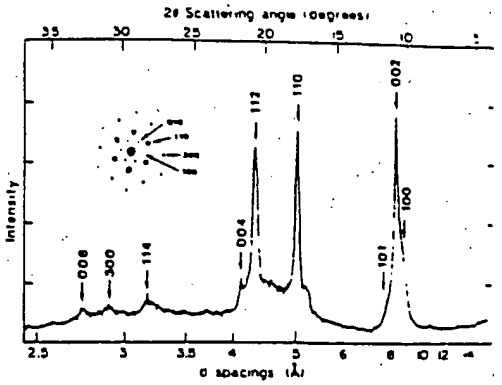

Figure 24. X-ray diffraction pattern of a microcrystalline powder of fullerene-60 obtained by Krätschmer, Lamb, Fostiropoulos, and Huffman.[4] Inset (upper left) is a single-crystal electron diffraction pattern (shown in more detail in Figure 25) indexed with Miller indices compatible with the X-ray pattern. This pattern provided unequivocal evidence that the C_{60} species they had isolated was a round ball 10 Å in diameter in perfect agreement with expectation for buckminsterfullerene (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

and London theory, calculated the ring current magnetic susceptibility and concluded that the shielding should be vanishingly small (less than 1 ppm) due to cancellation of the diamagnetic and paramagnetic contributions. They concluded that fullerene-60 should not show normal aromatic behavior. Studies by Fowler, Lazzeretti, and Zanasi[210] and Pauling[211] have suggested however that the diamagnetic term has been underestimated. From large scale ab initio, coupled Hartree–Fock calculations (involving all electrons) of the polarizability and magnetizability of C_{60} and C_{20}^{2+}, Fowler et al.[210] conclude that the shielding should be roughly the same as for related aromatic systems. Haddon and Elser[212] have discussed their own results[208,209] and reinterpreted those of Fowler et al.[210] and conclude that the latter study is consistent with a small delocalized susceptibility. Schmalz[213] has argued that the Fowler et al.[210] interpretation is correct. The NMR study of Taylor et al.[6] yielded a chemical shift for fullerene-60 which is fairly typical for an aromatic species. Fowler et al.[214] have extended their approach to the calculation of the shifts in fullerene-70, obtaining results consistent with observation and confirming the line assignments made by Taylor et al.[6] This problem is further discussed in section X.

IX. The Isolation, Separation, and Structural Characterization of Fullerenes-60 and -70

Almost five years, to the day, since the special behavior of the C_{60} signal was recognized (Figure 5) and the buckminsterfullerene proposal made,[3] macroscopic samples were isolated and characterized. Krätschmer, Lamb, Fostiropoulos, and Huffman,[4] in following up their earlier IR observations,[5,74] discovered that at ca. 300–400 °C a solid material could be sublimed from the deposit obtained from arc-processed graphite. They found that this sublimate was soluble in benzene and could be crystallized. The X-ray and electron diffraction analyses (Figures 24 and 25) of the crystalline material so obtained (Figure 26) showed it consisted of

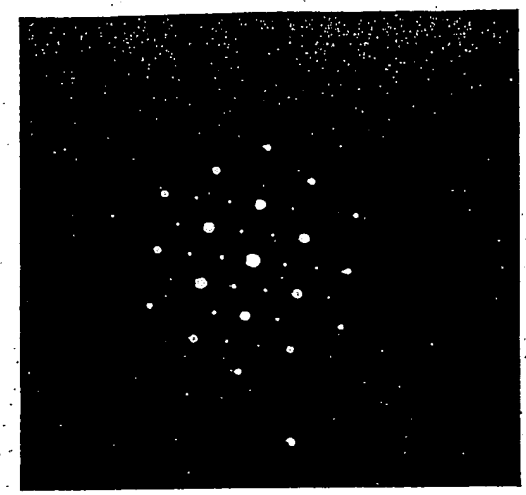

Figure 25. Single-crystal electron diffraction pattern of fullerene-60.[4] Further details of indices are given in Figure 24 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

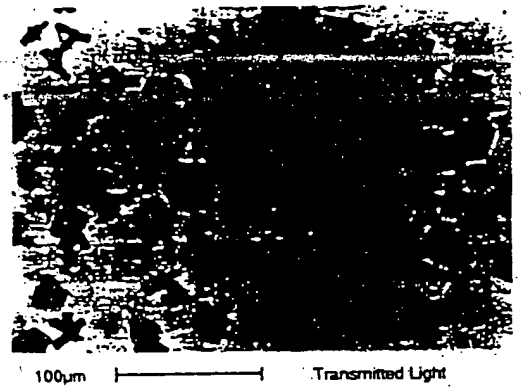

Figure 26. Transmission micrograph of crystals extracted by Krätschmer et al.[4] from the deposit of arc-processed graphite. Thin platelets, rods and stars of hexagonal symmetry are observed (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

by ca. 3.1 Å (in graphite the interlayer distance is 3.4–3.5 Å). These authors also reported IR (Figure 27), UV/vis, and mass spectra of the extracted material. Bands of C_{70} were present (weakly) in the IR spectrum and, in the UV/vis spectrum, some features of fullerene-60 were masked by those of fullerene-70. These results provided the first confirmation of the fullerene-60 structural proposal.

In a parallel and independent study of similarly arc-processed carbon, Taylor et al.[6] had also shown that C_{60} was present by FAB-sampled mass spectrometry and that a red soluble extract could be obtained by treating the carbon deposit directly with benzene. Taylor et al.[6] processed the extract by the Soxhlet procedure and obtained a material which mass spectrometry showed to contain a range of fullerenes, C_{60} and C_{70} in particular (Figure 28). This material was chromatographed by using hexane/alumina, and C_{60} and C_{70} were thereby separated into a magenta and red fractions, respectively. ^{13}C NMR measurements yielded a single line for C_{60} (Figure 29a), providing definitive

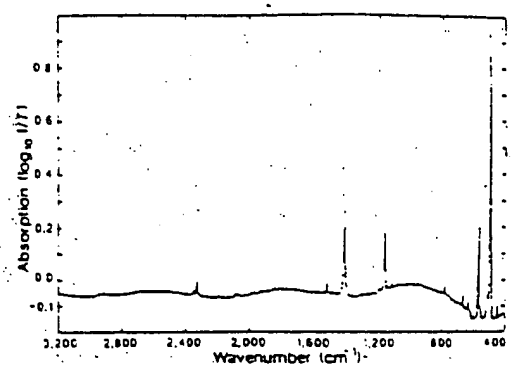

Figure 27. Infrared spectrum of fullerene-60 presented by Krätschmer et al.[4] showing the four fundamentals in excellent agreement with expectation for the proposed fullerene-60 structure. Weaker features belong to fullerene-70 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

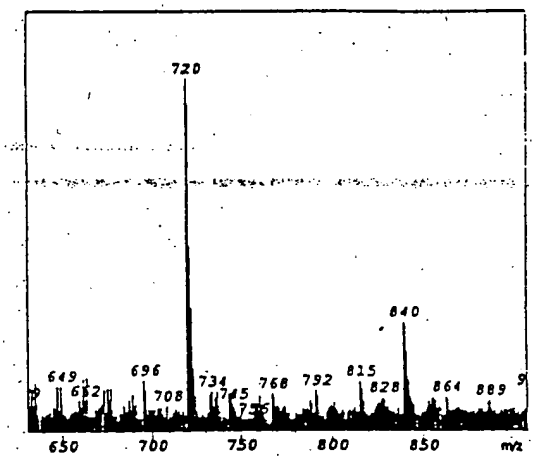

Figure 28. FAB-sampled mass spectrum, obtained by Taylor et al.[6] of the soluble material extracted from arc-processed graphite. Apart from unequivocal evidence for C_{60} and C_{70} in the extract there is also evidence for other even-numbered carbon species, particularly C_{84} and C_{88} (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

proof that all 60 atoms are equivalent—a result totally commensurate with the buckminsterfullerene structure. There is of course the alternative solution that all the atoms are located on the perimeter of a monocyclic ring. This (explosively) unlikely possibility was eliminated by the NMR spectrum of C_{70} which consisted of a set of five lines (Figure 29c) with a chemical shift pattern and relative intensities commensurate with the fullerene-70 structure (Figure 30b) first suggested by Heath et al.[7] This result not only confirmed the fullerene 5/6-ring geodesic topology but also eliminated the possibility that the carbon atoms might be fluxional. Almost as important is the confirmation, by this result, of the existence of other members of the fullerene family.

X. Postbuckminsterfullerene Research—The First Results

Since the revelation that macroscopic samples of the fullerenes can be isolated and that they are soluble and

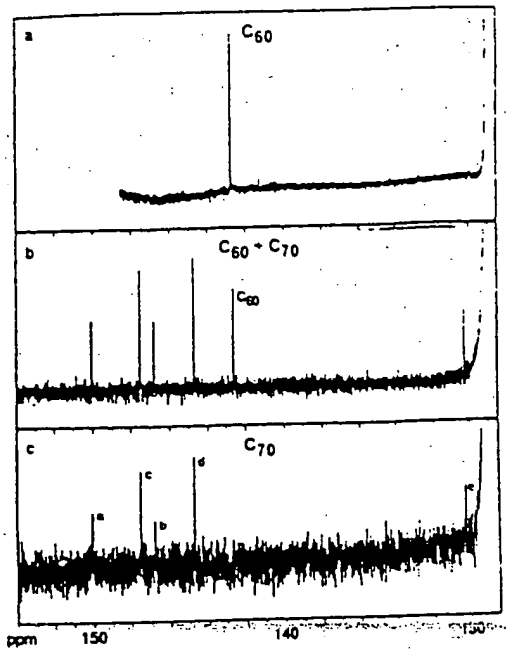

Figure 29. ^{13}C NMR spectra obtained from chromatographically purified samples (Taylor et al.[6]) of soluble material extracted from arc-processed graphite: (a) ^{13}C NMR spectrum of a purified sample exhibiting only a single resonance, (b) spectrum of a mixed sample, and (c) spectrum of a purified sample of C_{70} from which C_{60} has been eliminated. These spectra are consistent with the structures and assignments presented in Figure 20. The wing of the intense benzene solvent signal lies to the far right-hand side. This set of observations provided unequivocal evidence that the carbon atoms in C_{60} were indeed all equivalent in perfect agreement with expectation if the molecule were buckminsterfullerene (Figure 30). The five-line spectrum for C_{70} is also totally consistent with that expected for (D_{5h})fullerene-70 (Figure 30).[7] This spectrum eliminated any lingering doubt there might have been that the C atoms were either fluxional or perhaps located on the perimeter of a monocyclic ring. It also provided evidence for the stability of other members of fullerene family[1-6] (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

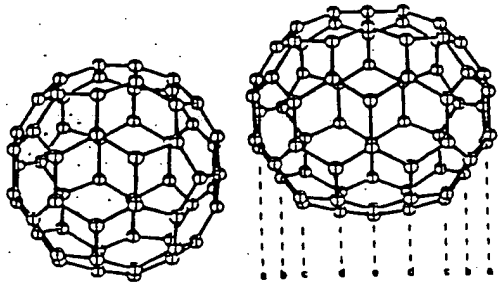

Figure 30. Schematic diagrams of fullerene-60 and fullerene-70 (based on diagrams of Slanina et al.[196]). All sixty atoms in fullerene-60 are equivalent whereas fullerene-70 possesses five different types of carbon in the ratios 10:10:20:20:10 in the order shown respectively as shown. Compare with the NMR spectrum shown in Figure 29.

chromatographically separable, it is now the turn of experimentalist to have a ball. Ajie et al.[215] and Hare et al.[216] have observed the UV/visible spectra of chro-

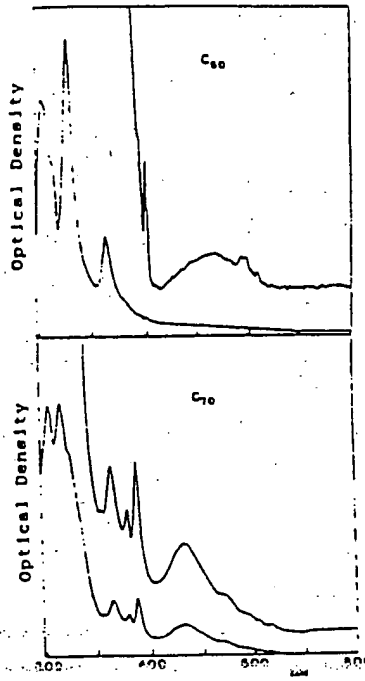

Figure 31. UV/vis spectra of chromatographically separated fullerene-60 and fullerene-70[215] in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

TABLE I. Properties of C_{60} Buckminsterfullerene

Vibrational Frequencies		
abs(obs)[a]	em(obs)[b]	calc, cm^{-1}[c]
528	527.1	472
577	570.3	618
1183	1169.1	1119
1429	1406.9	1434

X-ray Data[d,e]
r(C–C) = 1.388 (9) Å six–six ring fusion
r(C–C) = 1.432 (5) Å five–six ring fusion

NMR Data[f,g]
chemical shift (benzene soln) 142.68 ppm

Electronic/Spectroscopic Data	
electron affinity[h]	2.6–2.8 eV
ionization energy[i]	7.61 (0.02) eV
UV/vis bands[j,k]	213, 257, 329 (ϵ_{max} = 135 000, 175 000, 51 000) 404 (w) 440–670 (brd) (max. 500, 540, 570, 600, 625) nm

[a] Reference 4. [b] Reference 218. [c] Reference 191. [d] Reference 222. [e] See also Figures 24, 32, and 34. [f] See Figure 28. [g] Reference 6 (see also refs 215 and 228). [h] Reference 99. [i] References 101, 102, 239, and 240. [j] Reference 216 (see also ref 215). [k] See also Figure 31.

31). Reber et al.[217] have observed a luminescence spectrum. Frum et al.[218] have observed a most interesting IR emission spectrum from a hot gas-phase fullerene sample. The frequencies of the observed bands are given in Table I.

The availability of significant quantities of fullerenes has also opened up a Round Postbuckminsterfullerene Era of polycyclic aromatic chemistry. Haufler et al.[219] found that C_{60} can undergo Birch reduction to produce a white solid of formula $C_{60}H_{36}$. They point out that this formula is inconsistent with a pure hydrocarbon in

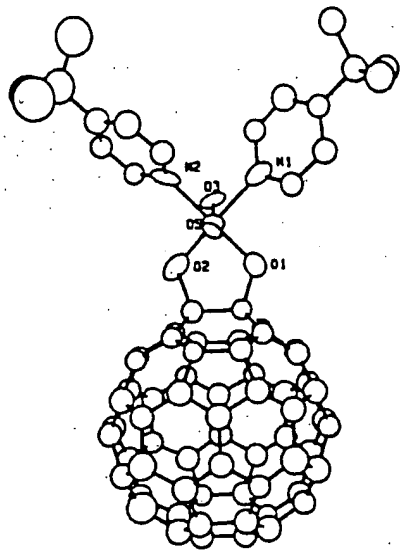

Figure 32. ORTEP drawing (50% ellipsoids) of the one-to-one C_{60}–osmium tetroxide adduct $C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2$ showing the relationship of the osmyl unit with the fullerene-60 carbon network[222] (reprinted from ref 222; copyright 1991 the American Association for the Advancement of Science).

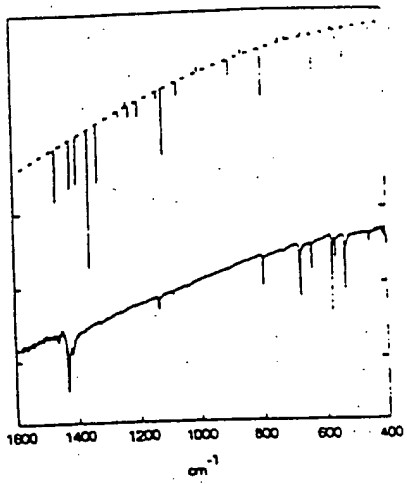

Figure 33. Infrared spectrum of chromatographically purified fullerene-70 obtained by Hare et al.[224] and compared with the calculated spectrum of Bakowies and Thiel.[198,199] The dashed curve is an estimated baseline. Note that the intensity of the very strong band calculated to lie near 1400 cm^{-1} has been arbitrarily reduced by a factor of 3 relative to other features. Features calculated to be very weak are indicated by markers above the estimated baseline (reprinted from ref 224; copyright 1991 The Royal Society of Chemistry).

which 12 isolated double bonds remain, possibly in the pentagonal rings. The reduction appears to be reversible. Evidence for the existence of a $C_{60}U$ complex was obtained by the laser vaporization approach, used originally to detect $C_{60}La$.[7] These authors also described the results of cyclic voltammetry measurements which indicated that C_{60} has two reduction potentials. Similar measurements have been made by Allemand et al.[220] who obtained a third potential. Their cyclic voltammetry measurements indicate that, curiously, fullerenes-60 and -70 appear to exhibit similar electrochemical behavior.

In one of the first attempts to introduce functional groups, Hawkins et al.[221] have found that they can form adducts of fullerene-60 with OsO_4(4-*tert*-butylpyridine) and its analogues. In a further study Hawkins et al.[222] have now obtained crystals of the osmium complex shown in Figure 32 and shown by X-ray analysis that rotation of the free C_{60} spheroids in the solid phase has been eliminated by the attached group. This study has yielded the first carbon–carbon bond lengths for the fullerene cage (Table I). Arbogast et al.[223] have observed fascinating photophysical behavior: fullerene-60 shows no fluorescence and efficiently catalyzes the formation of singlet oxygen. These authors observe a small S–T splitting of ca. 9 kcal/mol which is probably due to the large diameter of the molecule and the resulting small electron–electron repulsion energy. This together with the very low fluorescence rate and probably large spin–orbit interaction appears to account for the fact that intersystem crossing is a dominant process. Attention has been drawn to the fact that, due to their photophysical activity, care should be taken when working with fullerenes.

Hare et al.[224] and Bethune et al.[225] have made infrared measurements on chromatographically separated samples of fullerene-70 together with the calculated spectrum of Bakowies and Thiel[198,199] is presented in Figure 33. Bethune et al.[226] and Dennis et al.[227] have also made Raman measurements of fullerene-60 and -70. Liquid-phase NMR studies of unpurified fullerene mixtures by Johnson et al.[228] confirmed the result of Taylor et al.[6] (carried out on fully chromatographically purified samples) that the fullerene-60 resonance is a single line. Ajie et al.[215] have also confirmed the NMR measurements of a single line for fullerene-60 and five lines for fullerene-70; the former on a separated sample, the latter on a mixed fullerene-60/-70 sample. A 2D NMR analysis on fullerene-70 by Johnson et al.[229] has unequivocally confirmed the assignments made previously by Taylor et al.[6] shown in Figures 29c and 30b. Further refinements by Fowler et al.[214] of previous studies[210] predict fullerene-60 chemical shifts in excellent agreement with experiment (within 3 ppm). The study also includes estimates of the shifts for fullerene-70 so supporting further the pattern of line assignments given by Taylor et al.[6] (Figures 29c and 30b). Tycko et al.[230] and Yannoni et al.[231] have made solid-state NMR measurements down to 177 K where the motion is sufficiently slow for chemical shift tensor data to be obtained. Fullerene-60 rotates isotropically at 296 K and fullerene-70 rotates somewhat more anisotropically. Haddon et al.[232] have measured the magnetic susceptibility of solid samples of fullerenes and found it consistent with a molecule with a small ring current (see discussion in section VIII). Fowler[233] notes that when this result is compared and contrasted with the NMR shift of fullerene-60[6] it may imply ambivalent character when the question of the molecules "aromaticity" is considered.

Perhaps scanning tunneling microscopy (STM) offers more than any other a satisfying feeling of what the

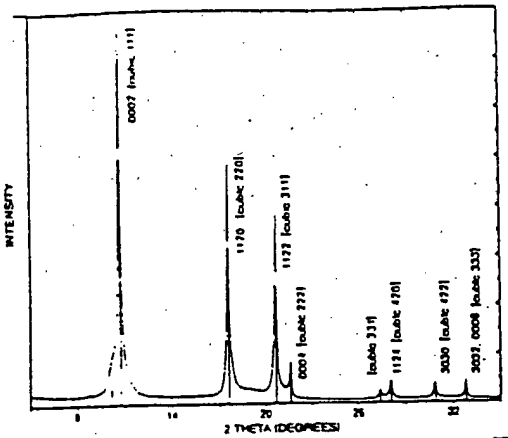

Figure 34. X-ray diffraction pattern obtained by MacKay et al.[227] from a chromatographically purified fullerene-60 sample. The structure revealed is basically that of a strongly disordered stacking of a simple hexagonal close-packing, exactly as for elemental cobalt. The hexagonal unit cell refines to $a = 10.017 \pm 0.004$ Å and $c = 16.402 \pm 0.01$ and contains two C_{60} spheres. The spheres would be 10.017 Å between centers and the calculated density would be 1.68 g cm^{-3}. The lines can be indexed as shown and it will be noted that, because of the stacking disorder, only those reciprocal lattice rows parallel to c for which $-h + k = 3n$ are present. The c/a ratio of 1.637 is very close to the theoretical value of 1.633 and thus the pattern can also be indexed with respect to a face-centered cubic lattice (with $a = 14.186$ Å) (as of copper metal) with stacking disorder which removes the 200 and 400 reflections and which introduces a very weak line (the first) at a spacing of $a/(8/3)^{1/2}$ due to double diffraction from stacking faults. The intensity variation of the pattern as a whole corresponds to the transform of a sphere of radius 3.5 Å giving a first minimum in the region of $2\theta = 25°$. Since the crystal is a mixture of FCC and HCP arrays, extracted crystalline material probably contains solvent molecules trapped in the faults.

et al.,[235] and Chen et al.[236] have deposited fullerene monolayers on gold and studied them by STM. The spherical molecules tend to form mobile hexagonally packed arrays on a surface. Chen et al.[236] observed local density variations on the surface of fullerene-60 which are highly suggestive of five- and six-membered rings.

The preliminary X-ray observations were made by Krätschmer et al.[4] working with crystalline material consisting mainly of fullerene-60 with some fullerene-70 present. A recent X-ray diffraction image was obtained by MacKay et al.[227] using chromatographically purified fullerene-60 (Figure 34). This image is commensurate with a completely random mix of HCP and FCC arrays of fullerene-60 molecules. Fleming et al.[238] obtained purely FCC structured crystals from vacuum sublimed material. The implication is that interstitially trapped solvent probably stabilizes the mixed FCC/HCP crystals. It appears that fullerene-60 spheres are rotating in the lattice[231] and that when rotation ceases at low temperature the crystals are still disordered at the atomic level.[221,222,238]

A most interesting study as far as theoretical chemistry is concerned is that of Lichtenberger et al.[239,240] who measured the photoelectron spectrum of fullerene-60 on a surface and in the gas phase (Figure 35). The results are in good agreement with the theoretical (DV)-Xα study of Hale[189] (Figure 23). The first IP of fullerene-60, 7.61 eV, is nicely consistent with the result obtained by Zimmerman et al.[101] and McElvany.[102]

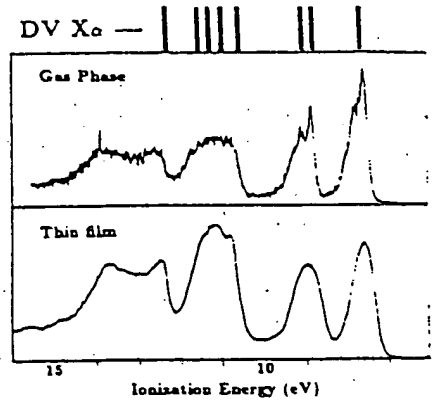

Figure 35. Gas phase (upper) and thin film (lower) He I valence photoelectron spectra of fullerene-60 obtained by Lichtenberger et al.[239,240] The DV-Xα results of Hale[189] (see Figure 23) which appear to be in good agreement with observation are indicated (reprinted from ref 239; copyright 1991 Elsevier Science Publishers).

Luffer and Schram[241] have made electron ionization mass spectrometric measurements on fullerene-60.

Several papers presented at a special symposium on the fullerenes (Nov 1990) have been collected together and published by Averback et al.[242] Some of the most important experimentally determined properties of fullerenes are presented in the Table I.

XI. Astrophysical Implications of C_{60}

Although low-temperature ion-molecule processes (Herbst and Klemperer[243] and Dalgarno and Black[244]) can account for most interstellar species, the long cyanopolyynes presented a problem. It was experiments which probed the possibility that carbon stars might be responsible for them[31,32] which revealed the stability of fullerene-60.[3] An important aspect of the experiments lay in the possibility of probing the conjecture of Douglas[40] that carbon chains might be responsible for the diffuse interstellar bands (DIBs). The DIBs are a set of interstellar optical absorption features of varying widths which have puzzled astronomers and spectroscopists since the mid-1930s. Herbig has published the definitive analysis of these features.[245,246] Many possible contenders for the carrier have been suggested, however no generally accepted explanation exists so far. This is strange as the species responsible is clearly abundant, chemically bound (i.e. not atomic), and must be quite stable in order to survive in the hostile interstellar environment or, if destroyed, be very efficiently reformed. The types of carrier appear to be few in number and must have very large electronic absorption coefficients.

The possibility that C_{60} might be the widely distributed in the Universe and particularly in the outflows from carbon stars was suggested when the original discovery of its stability was made.[3] It was also pointed out that the fullerene-60 surface might be an important site for the catalysis of interstellar reactions and perhaps it (*or a derivative*) might be responsible for such features as the DIBs. There is one key argument,[50,56-68] associated with the proposal that fullerene analogues (ionized or un-ionized, complexed or otherwise) may be

the carriers has that all previous suggestions do not: fullerene-60 and its analogues are unique in that they appear to survive the violent processes which occur when the atomic components of a chaotic plasma condense to form particles. Various aspects of this original conjecture, particularly with regard to possible derivatives such as intracage complexes both ionized and neutral, have been discussed[55-58] in general terms.

As far as the neutral fullerene-60 species in space is concerned, the negative results of searches based on the laboratory measurement[88] has been published by Snow and Seab[247] and Sommerville and Bellis.[248]

The conditions in the ISM are such that a large fraction of any fullerene-60 molecules present is likely to be ionized and thus it has been pointed out that the spectra of ionized fullerenes such as C_{60}^+ or fullerene analogues (such as the cage complexes $C_{60}M^+$) might be responsible for some astrophysical features.[55,57] Léger et al.[249] and Joblin et al.[250] have taken up the C_{60}^+ proposal and considered it further.

Complexed species (section VIII) in the interstellar medium are particularly interesting as any C_{60} present is likely to be ionized and probably have something stuck to its surface. As the DIBs exhibit features reminiscent of matrix spectra, the possibility that intracage complexes[55,57,201-203] as well as the extracage complexes[202] might be responsible has been discussed. Heymann[200] has considered the He intracage complexes and Ballester et al. other likely species containing O, Na, etc.[201] Kroto and Jura[202] draw particular attention to the fact that the charge transfer bands of the $(C_{60}M)^+$ intracage complex and the van der Waals extracage complex $(C_{60})^+ \cdot M$ (M = alkali, alkaline earth, or other element) are likely to be very strong. Particularly interesting are possible relationships that charge-transfer transitions might have with the DIBs and perhaps also the strong unassigned 2170 Å absorption feature which has puzzled astronomers for over seven decades. Hoyle and Wickramasinghe[251] suggested that C_{60} itself might explain this feature and further calculations relating to this possibility have been discussed by Braga et al.[167] Rabilizirov[252] has also discussed these possibilities. Wright[253] has discussed the general optical/UV characteristics of fullerenes and concludes that the observed interstellar extinction is not consistent with the presence of significant quantities of spheroidal particles with graphite-like outer shells. In this respect the existence of the amorphous carbon surface layers surrounding the graphite cores of carbon microparticles may well be important.[116] From the UV/vis spectra obtained so far[4,215,216] it is clear that neutral fullerene-60 is not responsible for either the DIBs or the 2170 Å hump.

There are also some intriguing interstellar emission features in the IR, termed the unidentified infrared bands (UIBs), which have been assigned to PAH-like material by Duley and Williams,[254] Léger and Puget,[256] and Allamandola et al.[256] The assignment rests largely on the reasonable correspondence between the astrophysical frequencies and those of polycyclic aromatic molecules which are usually used for fingerprint identification of large PAHs. Balm and Kroto[257] have discussed the fact that, if the fullerene-60 concept is correct, PAH material in space is likely to be nonplanar. They point out that one feature, namely that at 11.3

The new results also offer possible new avenues of study as far as condensed carbonaceous matter in the cosmos is concerned. According to McKay et al.[258] caged carbon clusters may offer a plausible explanation of some of the isotope anomalies observed in the elemental analysis of carbonaceous chondrites particularly the ^{22}Ne anomaly. Clayton[259] has pointed out that condensation in the atmospheres of supernovae might explain the so-called Ne-E anomaly. McKay et al.[258] have suggested that this observation might be explained by encapsulation of ^{22}Na in fullerene cages or icospiral embryos during the dust formation phases that follow supernova and nova outbursts. Subsequently, the decay of ^{22}Na yields an encapsulated ^{22}Ne atom. Zinner et al.[260] have pointed out that isotope anomalies are only to be found in spheroidal carbon grains. So far the only evidence that C_{60} might exist in space is an unconfirmed report by Anderson.[261]

XII. Conclusions

It took some 15 or so years before the imaginative theoretical conjectures of Osawa and Yoshida[12,14] and Bochvar and Gal'pern[17,18] were realized in the discovery of the stability of the C_{60} mass spectrometric signal[3] in 1985. A further period of five years elapsed during which time many experimental measurements and theoretical studies were made. By-and-large the theoretical work (section VIII) substantiated the idea that buckminsterfullerene should be stable. As time elapsed the weight of circumstantial evidence grew and ultimately became convincing. The key observations include:

(1) Detection of monometallic complexes indicated that atom encapsulation was feasible.[7,96]

(2) Further cluster beam studies showed 60 to be a magic number whether the carbon species was positively or negatively charged or neutral.[64,66,82]

(3) Reactivity studies showed the molecule to possess an inertness that was consistent with closure and the absence of dangling bonds.[103,96]

(4) The pentagon isolation principle explained the observation of C_{60} as the first magic number and C_{70} as the *second*.[8,9] Thus it was shown that the fullerene hypothesis rested on the observation of two magic numbers and not just one. Further refinement of the geodesic principle explained other observed magic numbers.[8,9]

(5) Large fullerene networks were found to possess quasiicosahedral structures and thus related giant concentric cage species[108] appeared to explain the infrastructure of the carbon microparticles observed by Iijima.[109,110]

(6) Photoelectron measurements of Yang et al.[99] were also quite consistent with the fullerene conjecture.

These and other studies (discussed in sections V–VII) thus had laid the background against which the critical infrared observation of Krätschmer et al.[5,74] was made. They were led to make this observation by considering that some intriguing optical features observed in 1982 might be due to buckminsterfullerene. These observations were followed up by Krätschmer, Lamb, Fostiropoulos, and Huffman[4] and Taylor et al.,[6] and the results have revolutionized the field in that now the material can be made in quantity and the properties of

It is interesting to note that the motives for the experiments which serendipitously revealed the spontaneous creation and remarkable stability[3] of C_{60} were astrophysical. Behind this goal lay a quest for an understanding of the curiously pivotal role that carbon plays in the origin of stars, planets, and biospheres. Behind the recent breakthrough of Krätschmer et al. in producing macroscopic amounts of fullerene-60, lay similar astrophysical ideas.[4] It is fascinating to now ponder over whether buckminsterfullerene is distributed throughout space, and we have not recognized it, and that it may have been under our noses on earth, or at least played an important role in some very common environmental processes, since time immemorial.

The material is already exhibiting novel physical and chemical properties and there can be little doubt that an exciting field of chemistry and materials science, with many exciting applications has opened up. One of its most important properties is its ability to accept electrons. The low-lying LUMO causes it to be a soft electrophile.

It is perhaps worthwhile noting that C_{60} might have been detected in a sooting flame decades ago and that our present enlightenment has been long delayed. How serious this delay has been only time will tell; however, already fullerene chemistry is a vibrant field of study and the prospects for new materials with noval properties is most promising. Certainly, a New Round Postbuckminsterfullerene World of carbon chemistry appears to have been discovered, almost overnight. It should not be long before the molecule becomes a standard in textbooks; indeed construction procedures for fullerene-60 and giant fullerenes are to be found in the educational literature.[125,262]

Warning

The UCLA group has pointed out the importance of treating the material with great caution at this time when so little is known about it.[263] Its ability to catalyze the formation of singlet oxygen and its novel chemical behavior inevitably suggest the possibility that the fullerenes might be carcinogenic. Particular care should be taken to ensure that the dust is not inhaled during preparation of the soot itself.

Acknowledgments. We are very happy to acknowledge the help of David Walton and Roger Taylor for helping to eliminate several obscurities from this article. We also thank Patrick Fowler for his help. Thanks are also due to all those who kindly sent reprints and we are grateful for permission to publish the data from several groups. S.P.B. thanks the SERC and AWA the Syrian Atomic Energy Commission for financial support.

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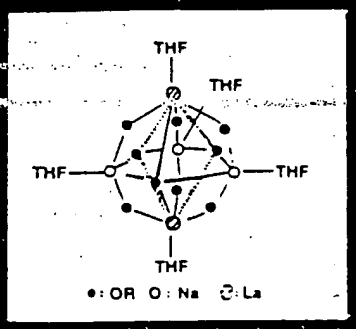
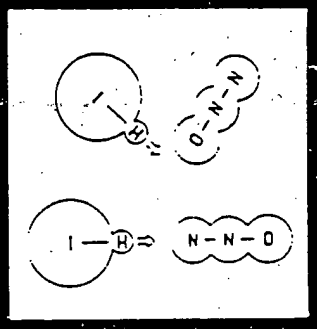
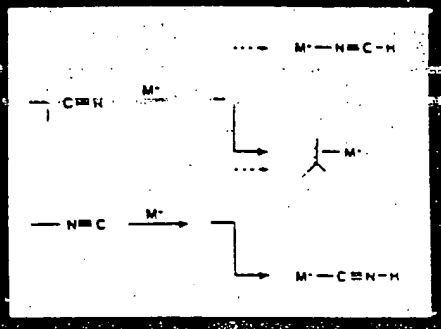
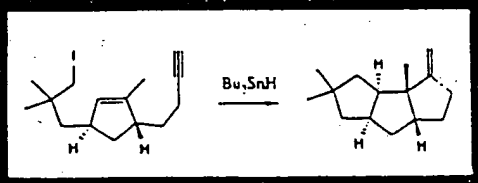
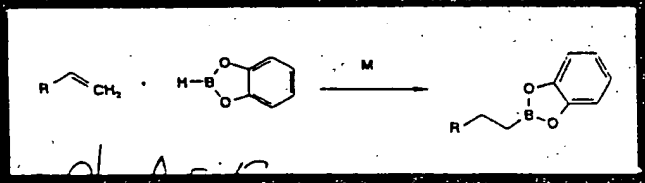
CHEMICAL REVIEWS

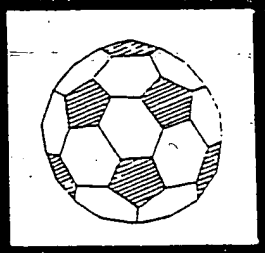


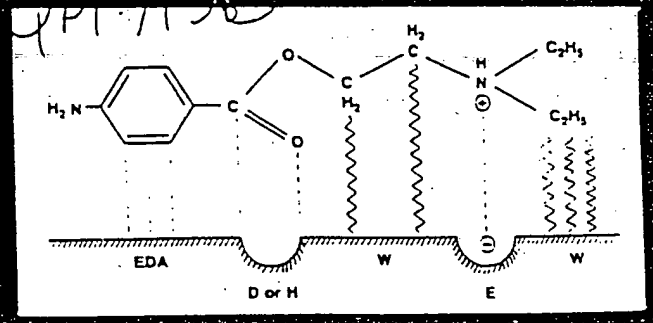












ANGEWANDTE CHEMIE

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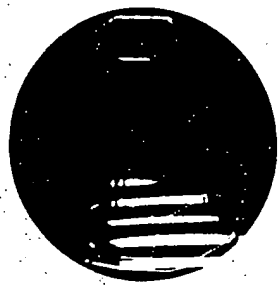
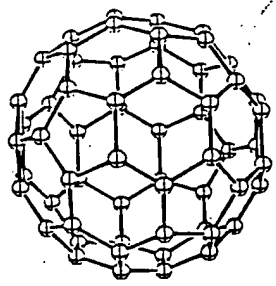
The cover picture shows a section of a high-frequency oven used in a novel synthesis of fullerenes. The reaction zone (at approximately 2800 °C, the light is dimmed by the soot beginning to deposit) is depicted at the start of the fullerene production. The inductor, boron nitride insulation tube, quartz tube, and initial formation of smoke can be seen. More about the novel efficient synthetic method is reported by M. Jansen and G. Peters on page 223. The boom in fullerene chemistry continues. The third in a series of highlights on the important recent results (previous updates were published last year in the January and June issues) will appear in the next issue. An overview of the preparations, properties, and reactions of C_{60} is planned. This issue includes two highlights on silicon clusters including Si_{60} (p. 173), a communication on $He@C_{60}$ (p. 183), and, last but not least, an exciting account by H. Kroto on the start of the fullerene story (p. 111).



Review Articles

A "round organic chemistry" has burgeoned this last year following the development of an efficient means of producing fullerenes in 1989/1990. One of the protoganists in the fullerene story describes in a lively personal style how this fascinating new chemistry came about. In this thriller he points out that the discovery of C_{60} in 1985 did not result from an applications-oriented search but rather from basic research and scientific curiosity.



C_{60}

H. W. Kroto*

Angew. Chem. Int. Ed. Engl. **1992**, *31*, 111...129

C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

Almost atomic resolution is achieved today in techniques for studying monomolecular Langmuir films of amphiphilic molecules. Synchrotron X-ray sources providing well-collimated, high-intensity radiation make this possible. In this review the principles and methods used to study thin films are discussed. In these investigations, for instance, a strong influence from solute molecules or ions in the subphase on the crystallinity of the monomolecular layer was revealed: whereas α-glycine increases the crystallinity of a fluorocarbon monolayer, β-alanine decreases it. Possible explanations for the phenomena are also presented.

D. Jacquemain, S. G. Wolf, F. Leveiller, M. Deutsch, K. Kjaer,* J. Als-Nielsen,* M. Lahav,* L. Leiserowitz*

Angew. Chem. Int. Ed. Engl. **1992**, *31*, 130...152

Two-Dimensional Crystallography of Amphiphilic Molecules at the Air–Water Interface

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C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

By Harold W. Kroto*

In 1975–1978 the long-chained polyynylcyanides, HC_5N, HC_7N, and HC_9N were surprisingly discovered in the cold dark clouds of interstellar space by radioastronomy. The subsequent quest for their source indicated that they were being blown out of red giant, carbon stars. In 1985 carbon-cluster experiments aimed at simulating the chemistry in such stars confirmed these objects as likely sources. During these cluster studies a serendipitous discovery was made; a stable pure-carbon species, C_{60}, formed spontaneously in a chaotic plasma produced by a laser focused on a graphite target. A closed spheroidal cage structure was proposed for this molecule, which was to become the third well-characterized allotrope of carbon and was named buckminsterfullerene. It has taken five years to produce sufficient material to prove the correctness of this conjecture. There may be a timely object lesson in the fact that exciting new and strategically important fields of chemistry and materials science have been discovered overnight due to fundamental research, much of which was unable to attract financial support, and all of which was stimulated by a fascination with the role of carbon in space and stars. In this account, interesting aspects of this discovery, its origins, and its sequel are presented. The story has many facets, some of which relate to the way scientific discoveries are made.

Molecules with Unsaturated Carbon Bonds

In the early 1970s, the chemistry of carbon in unsaturated configurations became the prime research focus for my group at the University of Sussex.[1] We were interested in free unstable species and reaction intermediates containing C-S, C-P, C-Si, or even C-C multiple bonds. The work originated from an abortive attempt to produce thioformaldehyde ($H_2C{=}S$) by photolysis. However, we switched immediately to thermolytic activation after I heard a lecture in which Don Johnson (from the U.S. National Bureau of Standards in Washington, D.C.) described how he and Powell had made this compound[2] by passing MeSSMe vapor through a quartz tube heated simply by a bunsen burner! This approach worked beautifully; we produced numerous other new compounds containing the C=S moiety such as thioethanal and thioketene by thermolysis of specially synthesised precursors, and characterized them mainly by microwave and photoelectron spectroscopy.[3] These sulfur species possessed a distinctive odor, and I for one have sympathy with the citizens of Freiburg who, according to Noller,[3] forced Baumann and Fromm to abandon their work on these compounds. We gave up our work on seleno analogues for similar reasons after detecting selenopropanal! After success with sulfur/carbon compounds we jumped, in the spirit of Mendeleev, to the next element in the second row of the periodic table, phosphorus. The first phosphaalkenes, $CH_2{=}PH$ and $CH_2{=}PCl$,[4] were produced in 1976 in a joint project with John Nixon; several more followed.[1] Simultaneously, Becker in Germany made $PhP{=}C(t\text{Bu})OSiMe_3$.[5] At this stage I envisaged a simple possible solution to the problem which had been on my mind

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since 1964, namely to ascertain whether derivatives of Gier's beautiful molecule HC≡P[6] could be made. I had been fascinated with HC≡P since the day I arrived as a postdoc at the National Research Council (NRC) laboratory in Ottawa and heard Takeshi Oka (who was then also an NRC postdoc) enthuse over a spectrum of this molecule which Kelvin Tyler (another NRC postdoc) had just obtained.[7] It seemed to me that the chemistry of HC≡P and its analogues must parallel that of the nitriles. Transition-metal complexes could probably be prepared, and cycloadditions to generate phosphorus-containing rings would be feasible.[8, 9] The simple approach worked very well, and we produced the first phosphaacetylene derivative, $CH_3C{\equiv}P$,[10] by thermolysis of $EtPCl_2$ (provided by R. Schmutzler). We followed this breakthrough with the syntheses of other XC≡P species (X = Hal, Ph, N≡C, N≡C−C≡C, etc.[11]). It is most satisfying that, as I had originally conjectured in 1964, the phosphaalkynes (and the phosphaalkenes) have subsequently been exploited by ourselves and other groups as synthetic building blocks.

In parallel with our studies of compounds made up of second-row elements and carbon we probed molecules containing chains with C−C multiple bonds. My fascination with such chains developed very early on in a study of the peculiar molecule, carbon suboxide O=C=C=C=O (one subject of my Ph.D. work at Sheffield in the early 1960s with my supervisor Richard Dixon). This stimulated my curiosity in extended carbon chains and the unusual flexibility which they often exhibited; a preoccupation with such molecules has continued to this day. When I flash-photolyzed C_3O_2 a year or two later at the NRC, I ended up with a cell full of black soot and a magnificent spectrum of the C_3 molecule, whose enigmatic patterns had finally been deciphered by Gausset et al.[11] Almost everything about these carbon chains seemed idiosyncratic, and I stored such observations up for the future. These memories were reawakened in the early 1970s by David Walton's work on polyynes at the University of Sussex. David had developed elegant methods for synthesizing long-chain polyynes, based upon silyl-protection techniques which he pioneered in acetylene chemistry.[12–14] He and his students had made the parent 24 carbon-atom species in minute quantities in solution and even a 32 carbon-atom (silyl-protected) polyyne.[13] These chains were precisely what was needed for a study of vibration–rotation dynamics—a topic which had attracted my interest. In my mind they conjured up an image of a microscopic quantum-mechanical cheerleader tossing a very bendy bamboo baton high into the air—and then attempting to catch the violently flexing and turning baton it as it descended. The obvious first compound for microwave study was the cyanopolyyne, HC_5N, because of its expected enormous dipole moment. Walton devised a synthetic route; Anthony Alexander, a "Chemistry by Thesis" student (editorial comment: for an explanation see the acknowledgements at the end of the review), successfully prepared it and measured its microwave spectrum in 1974.[15] This was a wonderful achievement for an undergraduate and a very important one for me, since it was the first molecule to be characterized on our newly acquired microwave spectrometer.

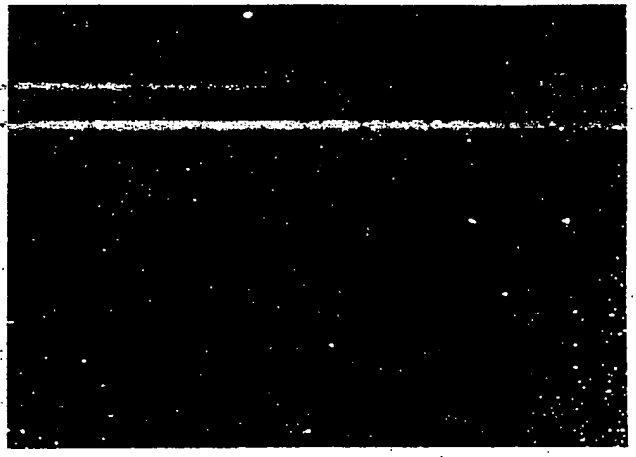

Fig. 1. The dark clouds in Taurus from Barnards 1927 survey. *Atlas of Selected Regions of the Milky Way*, (Ed.: E. B. Frost, R. Calvert), Carnegie Institute, Washington, D.C., 1927. Heiles's Cloud 2 is in the left-hand bottom corner as indicated by coordinate markers.

At about this time spectacular advances were being made in molecular radioastronomy. The black clouds which are smeared across our Milky Way galaxy (Fig. 1) were found to possess long-hidden dark secrets. Townes and co-workers[16] opened the Pandora's box in 1968 and revealed that the clouds are full of identifiable molecules. Astronomers suddenly realized what a key role molecules played in the

H−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−H

Harold Kroto, born in 1939, studied in Sheffield from 1958 to 1964 and received his Ph.D. for his research in the electronic spectroscopy of free radicals with R. N. Dixon. After three years of postdoctoral research at the National Research Council in Ottawa and Bell Laboratories, he started his academic career in 1967 at the University of Sussex in Brighton, where he became full professor in 1985. The most recent distinction Kroto has received is a Royal Society Research Professorship (1991). Since 1990 he has been chairman of the editorial board of the Chemical Society Reviews. His research interests include the spectroscopy of unstable species, carbon and metal clusters and microparticles, as well as interstellar molecules and circumstellar dust. Graphic design is his other passion.

intimate gas dynamics involved in the birth of stars and planets. Apart from well-known species such as ammonia, water, and ethanol—enough for 10^{28} bottles of schnapps in Orion alone—Bill Klemperer ingeniously identified the HCO^+ ion (protonated CO)[17] which had not previously been detected in the laboratory. Thus space served not only as a playground reserved for astronomers, but it now presented chemists with a novel piece of apparatus, indeed a colossal new spectroscopic sample cell, containing a plethora of exotic molecules in a wide range of physico-chemical environments.[18] Shortly after Turner[19] had detected HC_3N by microwave frequencies, I wrote to Takeshi Oka at the NRC; my group had recorded the analogous frequencies of HC_5N, and I wanted to search for the molecule in space. Takeshi and I had worked (1964–1966) in the same laboratory at the NRC during the golden years of that research organization.[*] He replied saying that he was "very, very, very, very, very much interested".

In November 1975 the search for radio waves of HC_5N (with Canadian astronomers Lorne Avery, Norm Broten, and John MacLeod) resulted in the successful detection of a signal from Sgr B_2, a giant cloud of molecules near the center of the galaxy.[20] Although we had been hopeful, we were surprised by our discovery since it had seemed such a long shot. In 1975 molecules with more than three or four heavy (C, N, or O) atoms were assumed to be far too rare to be detectable. However, having found HC_5N in space, we thought that HC_7N might also be present. Walton devised a synthesis of HC_7N, and graduate student Colin Kirby managed the very difficult problem of making it and measuring its spectrum.[21]. By the time Colin (in England) finally succeeded in recording the vital frequency, we were actually working on the radio telescope, since our allotted observing session had already started. Colin telephoned my wife, who wrote the value on an envelope (Fig. 2 left). She then telephoned Fokke Creutzberg, a friend in Ottawa, who also noted it carefully (Fig. 2 right) and transmitted it to us at the telescope site in Algonquin park (Fig. 3). The next few hours were high drama. We dashed out to the telescope and tuned the receiver to the predicted frequency range as Taurus (Fig. 1) rose above the horizon (perfect timing). We tracked the extremely weak signals from the cold dark cloud throughout the evening. The computer drove the telescope and stored incoming data, but to our frustration we could not process the data on-line while the telescope was running. The system did, however, display individual ten-minute integrations, and as the run progressed we watched the oscilloscope for the slightest trace of the predicted signal in the receiver's central channel. During the course of these ten-minute snapshots, we gradually concluded that the central channel signal was possibly higher on the average than nearby ones. Desperate for even the faintest scent of success, we carried out a simple statistical analysis in order to determine whether the signal level of the channel was greater than the noise. As the night wore on we became more and more excited, convinced that the signal was significantly more often high than low; we could hardly wait for Taurus to set. By 1:00 a.m. we were too excited and impatient to wait any longer, and shortly before the cloud vanished completely, Avery stopped the run and processed the data. The moment when the trace in Figure 4 appeared on the oscilloscope was one of those that scientists dream about and which, at a stroke, compensate for all the hard work and the disappointments which are endemic in life. The circumstances of this discovery—the arrival of the value of the microwave fre-

Fig. 3. The 46 m radiotelescope in Algonquin Park, Ontario, Canada with which the long-chain carbon molecules in space were detected.

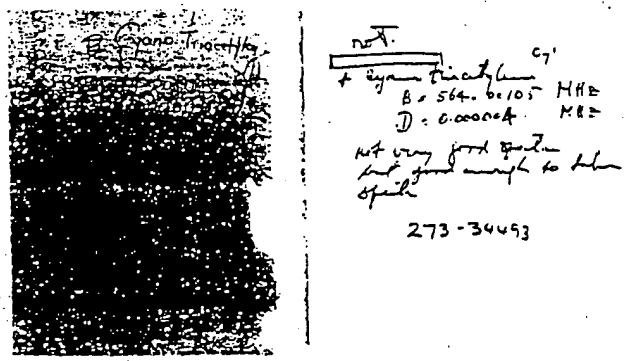

Fig. 2. The envelope (left) and intermediate note (right) with the precious experimental data from which the frequency of HC_7N in space was determined.

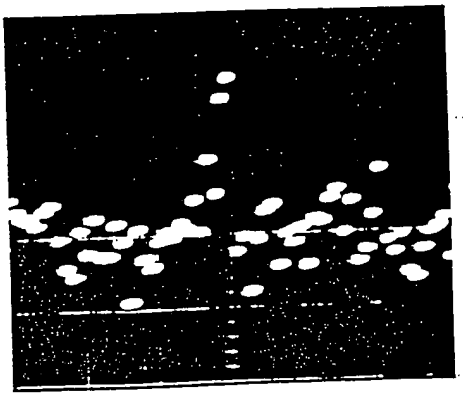

Fig. 4. The first oscilloscope trace of the radio signal emitted by interstellar HC_7N in Heiles's Cloud 2 in the constellation of Taurus (see the coordination markers in Fig. 1).

[*] Under the guidance of Gerhard Herzberg the NRC had become the Mecca for spectroscopists, and it was here that Cec Costain introduced me to the delights of microwave spectroscopy.

quency from the UK just in the nick of time, the gradual growth of the conviction that there might be a signal in that central channel of the receiver, and then finally the revelation that we (Fig. 5) had detected an enormous molecule in space[22]—made for a truly cathartic scientific experience. (Modern on-line data processing would have diminished the experience). Obviously, the next candidate was HC_9N, but

Fig. 5. The team at the NRC laboratory just after the detection of HC_9N in space (from left): Avery, Oka, Broten, MacLeod, and Kroto.

its synthesis was a daunting task. Fortunately, Oka developed a beautifully simple extrapolation technique with which he predicted the radio frequencies of HC_9N. Almost unbelievably, we detected this molecule as well![23] Bell et al. later detected even $HC_{11}N$.[24]

The Search for the Source of Carbon Chains in Space

It is not so obvious today, but in 1975–1978 such long-chain molecules were a totally new and unexpected component of the interstellar medium. How such species came to be present was not at all clear. I felt that it was not sufficient just to have co-discovered them: I really wanted to solve the puzzle of how they got there in the first place, and indeed what they were doing there anyway. After all, everything in nature seems to have some role to play. The search for the source of these compounds became something of a preoccupation (even an obsession). By the early 1980s I was convinced that the ion–molecule reactions which Eric Herbst and Bill Klemperer,[25] and Alex Dalgarno and John Black[26] had devised, and which accounted beautifully for almost all other interstellar molecules, really could not explain the origins of chain molecules.[1,18] It gradually became clear to me that red giant, carbon stars must hold the key. Particularly interesting was the spectacular infrared object IRC+10216, discovered by Eric Becklin and his colleagues,[27] which pumps vast quantities of chains and grains out into space. I wondered about this red giant and the fact that it was shrouded in grains and chains, which were formed at roughly the same time,[1,18] and whether "the long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2, and C_3, which are well known, and particles with high carbon content such as soot".[1] Perhaps some symbiotic chain/dust chemistry was involved.

The First Visit to Rice University (Easter 1984)

The foregoing account sets out the background for my thoughts about the role of carbon in space prior to my trip to Rice University in Texas during Easter 1984 to visit Bob Curl. Almost the first thing that Curl told me was that I should visit his colleague, Rick Smalley. He enthused over a very recent result obtained by Smalley and his co-workers, who had analyzed the spectrum of the SiC_2 and had shown the molecule not to be linear, as some might have expected, but triangular.[28] (The analogous C_3 species is linear, although only just.[11]) I visited Smalley's laboratory and saw the laser vaporization cluster-beam apparatus which he and his co-workers had recently developed. This powerful technique enabled the mass-spectrometric study of stable clusters formed in a helium-entrained plasma, produced by a pulsed laser focused on a solid target. In this particular experiment silicon carbide was vaporized and the electronic spectrum of SiC_2 observed.[28] I was much impressed by the result but even more by the experimental technique.[29] This method was clearly a major breakthrough in cluster science, since it made refractory clusters accessible for detailed study for the first time. I had already heard of it, but to see the apparatus in operation was quite fascinating. The result of the SiC_2 experiment was particularly interesting to me, because it was consistent with some unusual theoretical results for >Si=C< species[30] obtained at Sussex in collaboration with John Murrell some years earlier. What excited me most, however, was the thought that by simply replacing silicon carbide with graphite, it should be possible to simulate the type of chemistry which takes place in the atmosphere of a carbon star and produce the long carbon chains. As the day wore on I became more and more convinced that the technique was perfect for this purpose and that evening discussed it with Curl. Because of his interest in microwave spectroscopy, he was immediately enthusiastic, and we made plans for a joint project in the hope that Smalley would also be interested. Perhaps we could detect chains with as many as 24–32 carbon atoms related to Walton's polyynes or Hintenberger's equally amazing pure-carbon species (C_{33} etc.), which were detected by mass spectrometry in the early 1960s in a carbon arc.[31] I dreamt that one day it might be possible to detect a chain molecule such as $HC_{33}N$ (which is as long as the chains that Walton had made in a test tube) in space. Curl was particularly excited by the prospect that we could check out an interesting idea of the late Alec Douglas,[32] namely, that carbon chains might be carriers of the famous Diffuse Interstellar Bands—a set of absorption features[33] which have puzzled astronomers and spectroscopists for more than six decades. Because the project was not considered a priority by the cluster group at Rice University at that stage, it had to await a convenient slot in their program.

In the interim, a group at Exxon carried out the basic graphite-vaporization experiment. In the summer of that year (1984) they published a fascinating result: the discovery of a totally new family of carbon clusters C_{30}–C_{190}[34]—

much larger species than those prepared by Walton et al.[12-14] or observed by Hintenberger.[31] This exciting discovery was peculiar because only even-numbered clusters were detected. It is important to note that at this juncture no specific cluster was perceived to be special. In August 1985 (almost 18 months after my visit) Curl telephoned to say that carbon experiments were at long last imminent. He asked whether I wanted to come to Houston to participate or if they should carry out the experiments and send the data to me. One thing was certain in my mind: I had not waited this long to have my experiments carried out by others in my absence; I wanted to do them myself and to direct the operation personally. Therefore I packed my bags and at my wife Marg's expense arrived at Rice University within days.

Second Visit to Rice University—The Discovery of C_{60}

Silicon and germanium cluster studies were on the Rice plate in August 1985 because of their implications for semiconductors. Such experiments were considered to be important because the results might have useful applications (!) The carbon project, on the other hand, was thought to have no possible application (other than for astronomy) and was to be completed quickly, causing as little delay to the semiconductor study as possible. Preliminary measurents on carbon had already been carried out, and the Exxon spectra had been reproduced; nothing untoward was noticed. As soon as I arrived (August 28th) I presented a lengthy informal seminar on everything I knew about carbon in space, stars, and soot. My experiments started on Sunday, September 1st, 1985. I worked in the laboratory alongside two research students, Jim Heath and Sean O'Brien—an exhilarating experience; Yuan Liu was also involved. We toiled late into the night, varying the clustering conditions and monitoring the reactions of the carbon clusters with hydrogen, oxygen, and ammonia—gases which I thought would give rise to polyynylcyanides and other chain molecules. They did! The experiments thus immediately confirmed that the chemistry in red giant stars could be responsible for interstellar carbon chains. Curl and Smalley paid frequent visits to the laboratory. As the experiments progressed it gradually became clear that something quite remarkable was taking place: As we varied the conditions from one run to the next, we noticed that a peak at 720 amu[*] (corresponding to a C_{60} species) behaved in a most peculiar fashion. Sometimes it was completely off-scale; at other times it was quite unassuming. The spectrum recorded on Wednesday, September 4th, 1985 was astounding (Fig. 6). Our reactions were noted in the laboratory record book (Fig. 7a), and I annotated my copy of the printout (Fig. 6). From that point onwards the idiosyncratic behavior of this peak was followed very, very closely (Fig. 7b). When this result appeared, the carbon project—

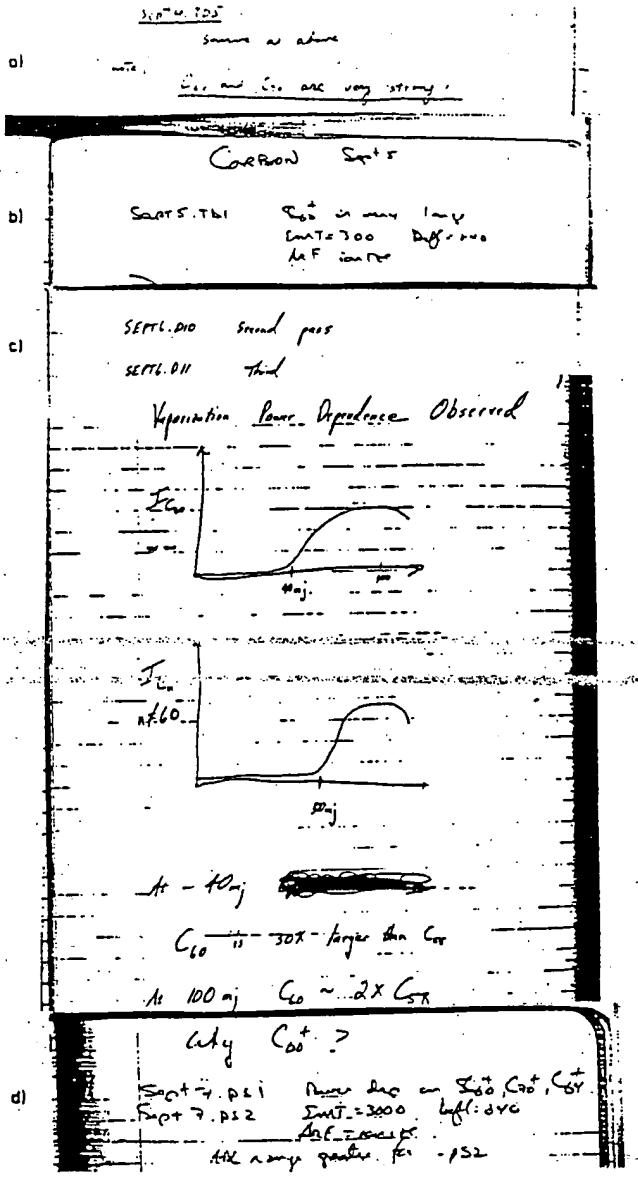

Fig. 7. Entries by Heath, Liu, and O'Brien in the Cluster Laboratory Notebook from the period September 4–7, 1985 when key experiments were carried out at Rice University. a) September 4th: First recorded note that C_{60} and C_{70} were very strong (see also Fig. 6). b) September 5th: C_{60} signal again very strong. c) September 6th: Record of first experiments which specifically aimed at optimization of the conditions for production of a dominant C_{60} signal ("C_{60} is 30 × larger than C_{58}.") d) September 7th: Further power-dependence studies.

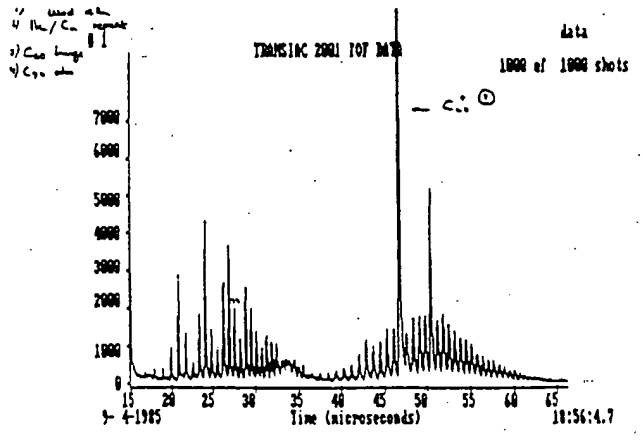

Fig. 6. Annotated time-of-flight (TOF) mass spectrum of carbon clusters produced on Wednesday, September 4th, 1985, the day on which the dominance of the C_{60} signal was first recorded (see also Fig. 7a).

[*] Editorial note: amu = atomic mass unit. According to *Quantities, Units and Symbols in Physical Chemistry* (Ed.: Int. Union of Pure and Applied Chemistry), Blackwell, Oxford, 1989 (Chapter 2.10), amu is the symbol for the unified atomic mass unit m_u and the unit u. In this review the unit amu which is still encountered frequently is used.

for the first time—engendered general interest, and by mutual agreement continuation of the semiconductor program was delayed so that we could concentrate on the remarkable phenomenon which we had uncovered. As the weekend approached our actions, thoughts, and conversations turned more and more to the phenomenon. What might this special "wadge" of carbon be? Smalley had never come across this British term for a cluster and liked it so much that he started to refer to C_{60} as the "Mother Wadge"; the omnipresence of the cluster led me to call it the "Godwadge". On Friday, September 6 during a group meeting, Curl suggested that we should concentrate on identifying the conditions under which the 720 amu peak was most prominent. O'Brien and Heath agreed to work shifts during the weekend. Experiments aimed specifically at optimizing the signal were carried out that same evening, and conditions were immediately found under which C_{60} peak was 30 times stronger than the adjacent C_{58} signal (Fig. 7c). After further optimization (Fig. 7d) the striking spectrum (Fig. 8) was finally obtained. C_{70} is also prominent!

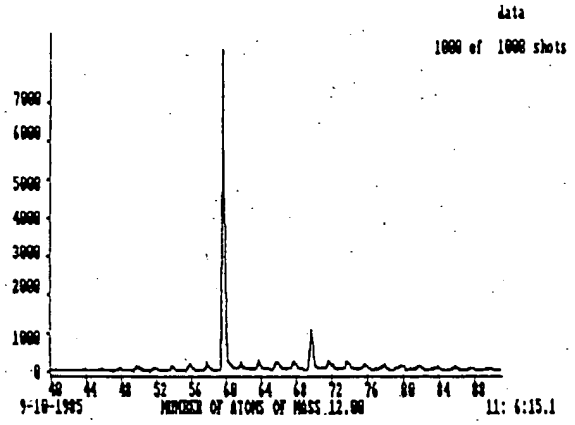

Fig. 8. TOF mass spectrum of carbon clusters under the optimum conditions for the observation of a dominant C_{60} signal.

The Structure of C_{60}(?)

What on earth could C_{60}(?) be? In the days following our discovery of C_{60} (Fig. 6), the signal began gradually to dominate our results as well as our thoughts and conversation. The quest for a structure which could account for this precocious wadge of carbon led to numerous, synergistic [Editorial comment: R. Buckminster Fuller's architectural constructions were based on a vectoral geometry which he called energetic—synergetic geometry. This was founded on a natural philosophy, according to which nature constructs systems of forces such that the maximal strength can be obtained from the minimum effort in construction.] discussions among all five members of the team during those days. The deliberations were particularly intense on Monday, September 9th. As this day wore on and all the ideas which had surfaced during the period were assessed and reassessed, a consensus grew that C_{60} might be some sort of spheroid. One possibility we considered was that the laser had blasted flakes of hexagonal carbon from the graphite surface, and that these hot graphite-like networks had somehow wrapped themselves up into closed cages, thus eliminating the dangling edge bonds and making the cage unreactive. This idea had instant appeal for all. For me this concept brought back vivid memories of Buckminster Fuller's geodesic dome at EXPO '67 in Montreal (Figs. 9 and 10). I had actually

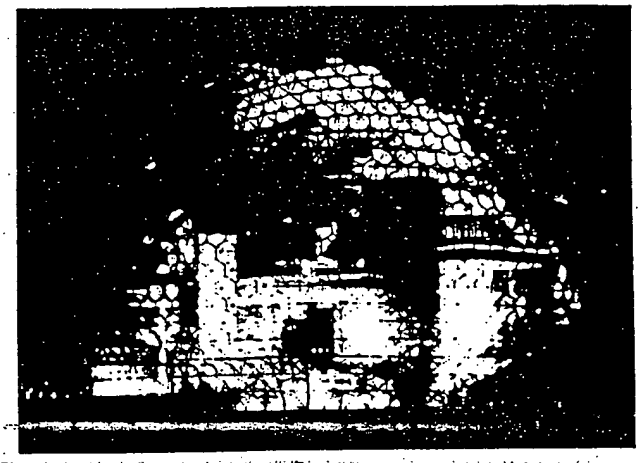

Fig. 9. Photograph (by Michel Proulx) of the geodesic dome designed by Buckminster Fuller for the U.S. exhibit at EXPO '67 in Montreal (taken from *Graphis* 1967, *132* 379). One of the pentagons necessary for closure is discernable in this photograph.

been inside this remarkable structure at that time and remembered pushing my small son in his pram along the ramps and up the escalators, high up among the exhibition stands and close to the delicate network of struts from which the edifice was primarily constructed. This experience had left an image in my mind which could never be erased. I had collected numerous photographs of the dome from magazines over

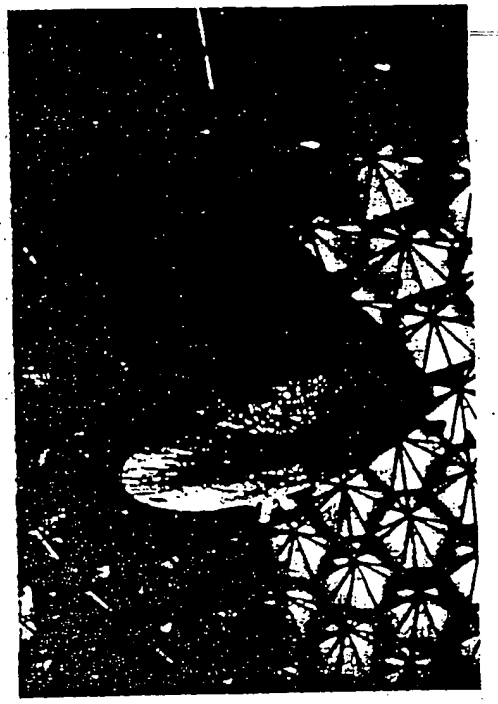

Fig. 10. Photograph (by Robin Whyman) of the inside of the EXPO '67 dome in Montreal. One of the pentagons necessary for closure is clearly visible in the middle section, as is the way in which the strut lengths have been adjusted to achieve a smooth round shape.

Fig. 11. The two cardboard polyhedra which played key roles in our search for the structure of C_{60} (see text). Left) stardome map of the sky (Buckminster Fuller patented icosahedral and other polyhedral world-map projections); right) Smalley's model with 60 vertices and 12 pentagonal and 20 hexagonal faces.

the years from Life, Paris Match, and Graphis. Particularly striking were those in my favorite graphic art and design magazine, Graphis, to which I had subscribed since my university days. As I remembered it, the Graphis pictures (Fig. 9) showed that the dome consisted of a plethora of hexagonally interconnected struts. Indeed, the dome had actually initiated my interest in some of Buckminster Fuller's other projects; I had even been in the process of writing to him with a view to working with him on the organized growth of massive urban structures. However, I did not pursue this, because I was offered a permanent academic position at Sussex at just that time.

As far as C_{60} was concerned, I wondered whether Buckminster Fuller's domes might provide some clue. Smalley also strongly favored some sort of spheroidal structure and suggested that we borrow a book from the Rice University library. We obtained a book by Marks[35] in which geodesic domes of all kinds were described. In addition I had one or two other structural proposals which intrigued me: One was a four-deck model 6:24:24:6 (two coronene-like sheets sandwiched between two benzenoid ones) with a roughly spheroidal shape. It contained 60 atoms, and its symmetry suggested that the dangling bonds might be somewhat deactivated. However, I really could see no reason why this species would be as unreactive as C_{60} appeared to be; a closed-cage solution would certainly be more stable. A second image came to mind several times, most vividly on this particular Monday. This was of a polyhedral cardboard stardome (Fig. 11 left) which I had constructed many years before when my children were young. This map of the stars in the sky was tucked away in a cardboard box (that universal quantum of storage) downstairs in my home far away in England. I itched to get my hands on it and even described its features to Curl at lunch time. I remembered cutting out not only hexagons but also pentagons. I wondered whether I should telephone my wife to ask her to count the vertices in order to ascertain whether, as I half-suspected, they totaled sixty.

The Mexican Restaurant

I was due to return to the UK the next day, so that evening (Monday, September 9th) I thought we should celebrate our extraordinary discovery. I invited the group out to dinner at what had become our favorite Mexican restaurant. During the meal the conversation was naturally dominated by C_{60}(?). We again considered all the ideas which had come up in our deliberations during the days that had passed since the signal had first been noticed. We agreed unanimously on a *closed cage* structure. We talked about Buckminster Fuller's domes, Smalley, about chicken-wire cages, and I reiterated the essentials of the stardome—its spheroidal shape, hexagonal faces, and, in particular, the pentagonal faces. Smalley expressed an interest. After the meal other members of the group went home; I returned to the laboratory in order to study the Marks' book on Buckminster Fuller, but I could not find it. I again considered telephoning home about the number of vertices in the stardome. But it was now far too late since it was well after midnight in the UK.

Very early the next morning Curl telephoned to say that Smalley had experimented with paper models based on the stardome characteristics I had mentioned the previous day. Smalley had come up with something bigger than anything he (Curl) had ever been involved with before. When I got to the laboratory and saw the paper model (Fig. 11 right) which Smalley had constructed during the night I was ecstatic and overtaken by its beauty. It seemed identical to the stardome as I remembered it, and I was quietly pleased that my conjecture had been right all along. Heath and his wife Carmen had also experimented with a geodesic structure modeled out of jelly beans and toothpicks; it was not quite so convincing.[36]

In summary, the quest for a rational explanation of the dominant line in the mass spectrum had reached a climax on Monday, September 9th. Ideas were suggested, refined, or critized in earnest throughout that final day. Buckminster Fuller's domes were invoked, Marks' book was consulted, and the stardome's pentagonal faces introduced at midday

and again in the evening; Smalley and the Heaths experimented further with models during the night after our meal. All this took place in a matter of hours, leaving no time for anything important—other than perhaps Marks' book—to "slip through the cracks".[37] It was most satisfying that synergistic (a Fullerism) teamwork had been involved in the experimental observation as well as in the positing of the structure.

I delayed my flight home for one extra day (until Wednesday, September 11th) in order to help to write the publication. At one point Heath was sitting at Smalley's desk when the telephone rang. A mathematician, whom Smalley had consulted earlier to ask about the structure, informed Heath, "Tell Rick—it's a soccerball!" Almost unbelievably, until that moment, none of us had realized that the C_{60} structure we were proposing had the same symmetry as the modern soccer-(USA) or football (rest of the world). I do not know how I could have been so blind—my only (feeble) excuse was that the modern football was introduced after I ended my serious soccer-playing days. The other members of the team could be excused, since a structure related to the American football really was an unlikely contender, at least at that stage. We immediately purchased a real football and our five-a-side team posed for a photograph (Fig. 12). I also

Fig. 12. The five-a-side Rice/Sussex football team (from left): O'Brien, Smalley, Curl, Kroto, and Heath.

photographed Smalley's paper ball (Fig. 11 right), but when I queried the whereabouts of the Heath model in order to photograph it for posterity, I was informed that it no longer existed because Mary-Joe (another Rice graduate student) had eaten it. So all tangible record of a truly remarkable edifice was lost for all time.

Since the geodesic dome concepts had played such an important part in helping us to arrive at the solution (at least as far as I was concerned), I suggested that we name the compound buckminsterfullerene. Smalley and Curl fortunately agreed, accepting that though the name was long, it did indeed roll smoothly off the tongue. Thus we avoided the fearful international conflict over terminology which would have raged had we named it after a certain well-known ball game. Smalley could not resist putting some alternative suggestions for names at the end of the publication. The name engendered the occasional mild criticism[38] which was dispatched with a little help from Shakespeare.[39] Now that some time has passed, it is satisfying to note how instructive (about geodesy) others have found the name and how flexible it has turned out to be. The whole family of closed cages can be appropriately named—fullerenes.[40] The paper[41] was dispatched by Federal Express to the journal *Nature* on the afternoon of Wednesday, September 11th, 1985.

Five Long Years in the Desert

The ten-hour nonstop flight home to England was a physical and psychological high for me. My first action upon entering the house was to open the cardboard box and take out the stardome which had influenced my deliberations during the search for the structure of C_{60}. It had always looked beautiful; now it positively glowed. When the news of our result spread, Martyn Poliakoff at Nottingham wrote that his friend, David Jones, had already thought of hollow carbon cages. In 1966 Jones had written a delightful article under the pseudonym Daedalus in the journal *New Scientist*[42,43] in which he had suggested that the high-temperature process in the production of graphite might be modified to generate graphite balloons. This was a typical example of the presciently "crazy" ideas of Jones. I thus learned about the Euler principle, which says that 12 pentagons are needed to close a network and that hexagons alone just will not do. I was introduced to D'Arcy Thompson's elegant book[44] and learned that one could close an even-numbered carbon cage with any number of hexagons (except one, I subsequently learned) provided 12 pentagons were included in the network. The beautiful Aulonia (Fig. 13 photograph from Tibor Tarnai) already knew more than we about these simple (pentagonal) facets of (its) life. This was all fun and truly

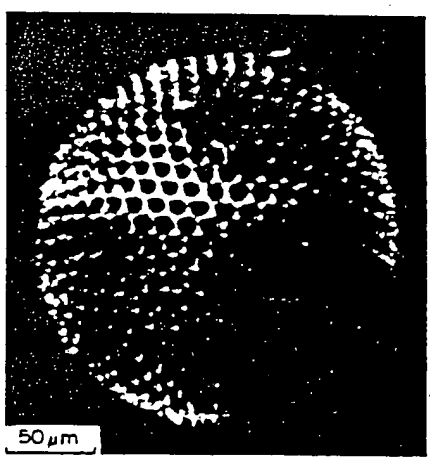

Fig. 13. A siliceous sea creature, *Aulonia hexagona*, appears at first glance to possess a skeleton composed completely of hexagons. Pentagonal structural elements are discernable, however (photograph supplied by Tibor Tarnai).

fascinating, because it became clear that there might even be other (even-numbered) carbon cages—there were certainly other (even-numbered) peaks (Fig. 6), in particular C_{70}. O'Brien and Smalley reached the same conclusions independently. Particularly important were a series of reactivity ex-

periments carried out by O'Brien, ... showed that all the even-numbered carbon species were totally unreactive, a result neatly commensurate with closed structures for all the even-numbered cages.[45]

I met David Jones, a most fascinating individual, who epitomizes so much of what the spirit of science should be about. We also learned that Osawa and Yoshida had already thought of C_{60} in 1970 and had even suggested that it might be superaromatic.[46, 47] In 1973 Bochvar and Gal'pern[48] also published a theoretical paper on the molecule. Thus it transpired that although there were some most imaginative scientists around, few—other than Orville Chapman at the University of California at Los Angeles (UCLA)[49]—had noticed these pioneering flights of imagination.

Circumstantial Evidence for the Identity of the "Third Man"

The first question stimulated by the realization that we might have found a "third form of carbon" with a hollow, cage structure was obvious: is it possible to trap an atom inside the cage? My early Sheffield background led me to wonder whether iron might form an intriguing ferrocene-like analogue. The day I left, Heath tried to encapsulate iron without success, but the next day he succeeded in detecting a stable $C_{60}La$ complex.[50] This experiment provided the first convincing piece of evidence to support our proposal of the cage structure. Then began what was to become a truly exhausting schedule for me: Every four to six weeks I flew to Houston, and after two to three weeks' work with the group at Rice I returned to the UK and my commitments in Sussex. As soon as I arrived in Houston I would present a group seminar based on ideas which I had developed while in the UK. This schedule continued until April 1987. From the outset the joint Rice/Sussex follow-up program had two clear objectives. First, to make enough C_{60} to prove beyond doubt that our structure was correct and second, to measure the optical spectrum of C_{60} which we had surmised might in some way be responsible for the Diffuse Interstellar Bands.[41] These astronomical features had of course been partly responsible for the carbon-cluster experiment in the first place. These goals were all-consuming and we often talked about "the little yellow (Smalley's guess) or pink (my guess) vial" of C_{60}.

During the late 70s and early 80s I felt that it was simply not enough just to detect the carbon chains; the source must be tracked down. This obsession with the source led ultimately to the discovery of C_{60}. After 1985 I developed a similar attitude to C_{60}. Our discovery of a species which probably had a truncated icosahedral structure was "not enough", and as months and then years passed, confirmation of the structure and its identification in space also became somewhat of an obsession. We (the Rice group and myself) were convinced from the outset that our proposed structure was correct; surely it was too beautiful and perfect to be wrong. However, if for once aesthetics were misleading us, it would be much better if we proved our model wrong ourselves. It is certainly fair to say that the proposed structure was greeted with scepticism by some; though many loved C_{60} and were convinced that we were right from the start. During this period (1985–1990) I examined the problem independently at Sussex, as well as in collaboration with the Rice group, who also made independent studies. In time all these efforts resulted in a mass of convincing evidence in support of our proposal.

From the moment we discovered that C_{60} was stable I had one all-consuming dream: I wanted so solve the molecule's structure by NMR spectroscopy. Because all 60 carbon atoms in buckminsterfullerene are equivalent, the ^{13}C NMR spectrum should consist of a single line. Proof of our radical proposal in such an exquisitely simple manner was to remain elusive for some five years; this goal was almost like a holy grail—far, far beyond reach. I was quite convinced that a clever young organic chemist would accomplish this task. I had one consoling thought, namely that we had been rather successful in the past with a series of molecules whose identifications were based on spectra consisting of single lines: Phosphaethene, $CH_2{=}PH$ (the first phosphaalkene made) had been assigned by its $J = 1 - 0$ microwave line[1, 4] and HC_5N and also HC_7N had both been originally single radioline detections in space.[20, 22] Then there was, of course, the 720 amu peak in the mass spectrum of C_{60}.[41] How fitting it would be to round it all off by *proving* by another *single* line that C_{60} was buckminsterfullerene.

C_{70} and the Fullerene Family

It is fair to say that I (and perhaps also my colleagues at Rice University) occasionally woke up in the middle of the night and wondered whether I should have to commit suicide if our idea turned out to be wrong. Had we stuck our necks out too far? These thoughts only lasted seconds. I would reassess all the evidence, realize that everything fitted, and go back to sleep convinced more than ever that C_{60} had to be a geodesic cage. Time pased, we made several advances,[51, 52] and each time the cage concept clarified our observations. That was important. I remembered hearing Richard Feynman on BBC radio say that it seemed to him that if a radical new theory were right, it would allow the solution of previously unsolved puzzles. I quantified this: If an idea fitted 80–90% of the observations, it was almost certainly right; if more than 10–20% of the details had to be bent to fit, it was almost certainly wrong. Buckminsterfullerene was well up in the first category.

I remember vividly the day on which all my lingering doubts vanished. I was sitting at my desk thinking about the reasons why C_{60} might be stable. The missing piece of evidence in this personal jigsaw puzzle turned out to be so simple, it was almost child's play; indeed it evolved from my playing with molecular models of various conceivable cages. The solution was related to the C_{70} signal which always popped up prominently when C_{60} was strong. I used to call the two species "the Lone Ranger and Tonto"[*] because

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they were so inseparable and because C_{60} was always dominant (Figs. 6 and 8). As far as C_{60} was concerned, it seemed no accident that the modern soccerball with the same layout is one of the most, if not *the* most, resilient of constructs, able to survive being kicked around the world (and perhaps around the galaxy). Maybe the football held a simple clue. When I looked carefully at a football, I was struck by the fact that all the (black) pentagons are isolated, whereas all the (white) hexagons are linked. It is known that unsaturated compounds composed of abutting pentagons (the pentalene configuration, Type II, Fig. 14), without substituents which allow extended conjugation, tend to be unstable. Curiously, a compound with just such a structure appeared on the cover of *Angewandte Chemie* (July 1987) that very week.

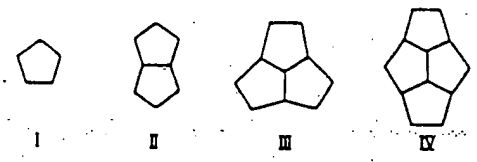

Fig. 14. Isolated and abutting pentagons: I, isolated; II, fused pair (pentalene configuration); III, symmetrically fused triplet (triquinacene configuration); IV, directly fused quartet [53].

Since Euler's law requires 12 pentagons for closure, it was also clear that C_{60} was the smallest carbon cage for which all the pentagons could be isolated. O'Brien's reactivity experiments had convinced us that closure was possible, even probable, for all the even clusters. I conjectured that a *pentagon isolation rule* could be formulated to account for the stability[53]; then I began to wonder which was the next cage for which pentagon isolation was feasible.

By playing with the models I saw immediately that it was not C_{62}, and as I added more atoms, try as I would, I could not find cage structures for C_{64}, C_{66}, or C_{68} without abutting pentagons. We had already proposed a structure for C_{70},[50] after Smalley had shown that by splitting C_{60} into two C_{30} hemispheres a ring of ten extra carbons could be neatly inserted, producing a most elegant, symmetric, egg-shaped structure (Fig. 15 right). Suddenly I realized that perhaps this C_{70} cage was the next structure after C_{60} which could close and which also had *isolated* pentagons (Fig. 15). This surprised me. Perhaps closure *necessitated* that 70 be the second magic number! We had stuck our necks out with the C_{60} hypothesis on the basis of a single peak in the mass spectrum, but it now seemed that the cage concept positively insisted that C_{70} *as well as* C_{60} are special.[53] That would be wonderful. A second solution which required both of these particular magic numbers was impossible to conceive, especially since 70 would be an unusual number to be deduced as magic at all, let alone the second in order. I knew that nature would not be that perverse, and thus for first time my conviction that our structure was corrrect became absolute, and I never again doubted that one day we would be vindicated. Indeed in my opinion this result meant that we were home and dry.

I was elated by this line of reasoning, but I really needed proof. I remembered that Tom Schmalz and his colleagues, Klein and Hite, in nearby Galveston had published some elegant graph-theoretical studies on the fullerenes. I contacted him and asked him what he thought about my idea. I was amazed and delighted when he told me that they had been looking at this same problem and had proven that cages composed of 62, 64, 66, and 68 atoms cannot be constructed without abutting pentgagons.[54] So it was true! I told him that I wondered whether the semimagic C_{50} might be the smallest cage able to avoid abutting triplets of pentagons (Type III, Fig. 14, Lit.[53]). Schmalz et al. subsequently showed this also to be correct.[54] One Sunday afternoon, sitting in front of the molecular models strewn all over our coffee table at home, I decided to investigate other semimagic numbers. I wondered about C_{32} which had been shown by the group at Rice University to be the first cage relatively stable towards photolysis. I toyed with the idea that it might be the smallest cage able to avoid fused quartets of pentagons (Type IV, Fig. 14). I tried to make the smallest model containing such a structure, and as I counted up the atoms I suddenly realized, that it was not C_{32} but a delightfully symmetric C_{28} cage (Fig. 16). I became excited because I knew, that during the Rice/Sussex collaboration period we had occasionally obtained mass spectra in which C_{28} was almost as dominant as C_{60}. At this point it seemed that essentially all the magic numbers would fall into place if these clusters were *all* cages. In particular, I found that I could explain the fascinating spectrum (Fig. 17) published by the Exxon group.[55] Here was all the proof I needed to convince myself that a whole family of cage molecules was sitting around waiting to be discovered. The first somewhat

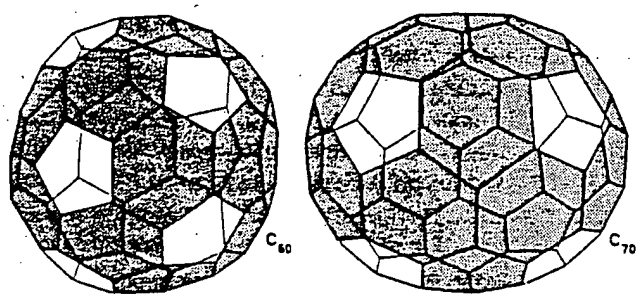

Fig. 15. For species with less than 72 atoms these two structures are the only ones which can be constructed without abutting pentagons. Thus on the basis of the *pentagon isolation principle* and geodesic considerations C_{60} and C_{70} are predicted to be the first and second magic fullerenes. This result together with Figure 8 provided the simplest and strongest circumstantial evidence supporting the closed-cage concept.

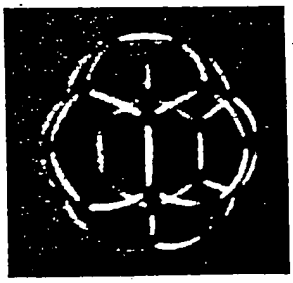

Fig. 16. Molecular model of C_{28}, one of several fullerenes (with 24, 28, 32, 50, and 70 atoms) predicted to be stable on the basis of geodesic and chemical considerations [53]. These magic-number predictions fitted almost perfectly the observations made under certain clustering conditions [51, 55] (see Fig. 17).

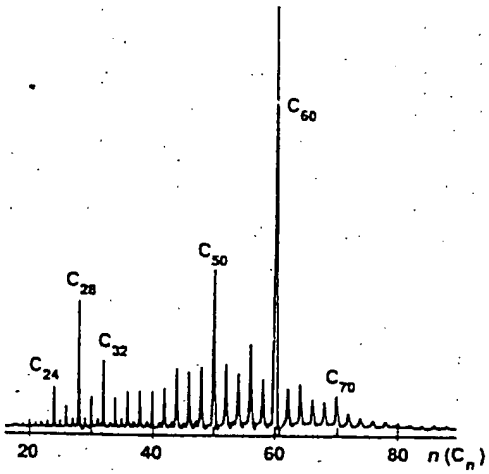

Fig. 17. The particularly interesting mass spectrum of C_n clusters obtained by Cox et al. [55]. The correspondence with the magic fullerene sequence 24, 28, 32, 50, 60, and 70 [53] was the most convincing evidence for the existence of the fullerene *family* prior to the extraction breakthrough. The sharp cut-off at 24 is particularly convincing, since no C_{22} fullerene can exist.

stable member of the family appeared to be C_{24}. This can be explained by the fact that C_{22} cannot exist (I am indebted to Patrick Fowler for pointing out this fact to me) and that C_{20} is the smallest cage and as it has no hexagons at all, almost certainly the least stable. To some extent C_{28} (Fig. 16) became my own personal favorite, because regardless of which of the four threefold axes one views this tetrahedral molecule along, it looks uncannily like Gomberg's famous free radical, triphenylmethyl; this also just had to be right. I knew about Moses Gomberg's discovery from my favorite organic text (Fieser and Fieser[56] which Harry Heaney, my chemistry teacher in school, had encouraged me to buy and read so long ago). It had always amused me to think that on attempting to make the rather mundane compound hexaphenylethane, Gomberg failed (miserably), produced the triphenylmethyl radical, and had to be consoled with becoming known as the father of free radical chemistry instead. This was the sort of "failure" that really appealed to me. If C_{28} is relatively stable, then $C_{28}H_4$ should be a fairly stable hydrofullerene. This seemed not at all farfetched; after all, dodecahedrane which Paquette and co-workers first made[57] is basically the perhydrofullerene of dodecahedrene (fullerene-20), the simplest and probably the least stable of all the fullerenes since it contains no hexagons. At this time I had a telephone conversation about nomenclature with Alex Nickon in which we came to the conclusion that the name "fullerenes" would work well for the family of carbon cages.[40, 53] I gained much satisfaction from the refined concept which was even more appropriate, because Buckminster Fuller had patented constructs of all shapes and sized based on the 5/6 ring principle;[58] some were very similar to the elongated framework of C_{70}. Nickon was just finishing his entertaining book with Silversmith on the origins of the trivial names of compounds.[40]

In Houston a particularly important series of experiments was carried out by Curl, Smalley, and their co-workers which offered further overwhelming evidence for closed cages.[52] One of these was a photofragmentation experiment which provided even-numbered products. Curl had worked out a neat way of explaining how the cages might "spit out" even-numbered (2, 4, 6, ...) carbon chains and then reseal.

Another most convincing study showed that when the encapsulation of atoms of various sizes appeared to be successful, the smallest caged species detectable had diameters commensurate with the known sizes of the encapsulated atoms.

C_{60} and Soot

During one of my eight visits to Rice University between August 1985 and April 1987 we considered carefully the reactivity results and developed a hypothetical mechanism for the formation of C_{60}.[45] Heath, O'Brien, and I spent hours in the library digging through an excellent selection of books and journals on carbon. The final version of the mechanism grew out of intense synergistic group discussion. It was also clear that the mechanism might explain soot formation as well. After all in a review on soot, Harris and Weiner[59] had pointed out the complete absence of knowledge of the chemistry involved in soot formation. Thus a fresh idea probably would be welcome. Our mechanism implied C_{60} should be a by-product of soot formation. Curl was apprehensive about introducing the word soot, especially in the title. How prescient were his worries! However, Smalley and I decided to throw caution to the wind—after all, when you have gone as far as you can go (in postulating C_{60} formation in a chaotic plasma), you might as well go further. Our paper met with some criticism.[60] To our delight, however, in 1987 we heard that Klaus Homann's group in Darmstadt discovered that C_{60} was a dominant ion in a sooting flame.[61] (Note: Very recently, a careful study by Howard's group at the Massachusetts Institute of Technology has shown that up to 7% of the soot from a benzene flame consists of fullerenes.[62])

The Giant Fullerenes

One day I decided to spend £300 on ten-thousand sp^2 carbon atoms (molecular models!) The odd eyebrow was raised at Sussex when I said that I was buying them just because I wanted to see what giant fullerenes such as C_{6000} (with a diameter ten times that of C_{60}) looked like. Ken McKay (a graduate student) obtained Coxeter's book[63] and Goldberg's paper[64] and set to work. When he came into my room with models of C_{240} and C_{540} (Fig. 18), I was delighted but perplexed—they were beautiful, but not at all what I had expected. C_{540}, in particular, was not round like Buckminster Fuller's domes, but in fact much more interesting: It was essentially a monosurface which swept between cusps in the vicinity of the pentagons; it had icosahedral symmetry, but was not an icosahedron.[65] Then we realized that its shape might explain[65] the polyhedral patterns in graphite microparticle electron microscope pictures published by Iijima (Fig. 19).[66] The structure of these microparticles could be nicely explained as concentric shells of graphitic carbon in which the shells had giant fullerene shapes. Few of our discoveries have delighted me more than these objects, partly because they are so elegant, but also because the exercise, which was started *purely* for fun and with no serious aim, had yielded such an apparently important result. It was also an object lesson, since I had assumed

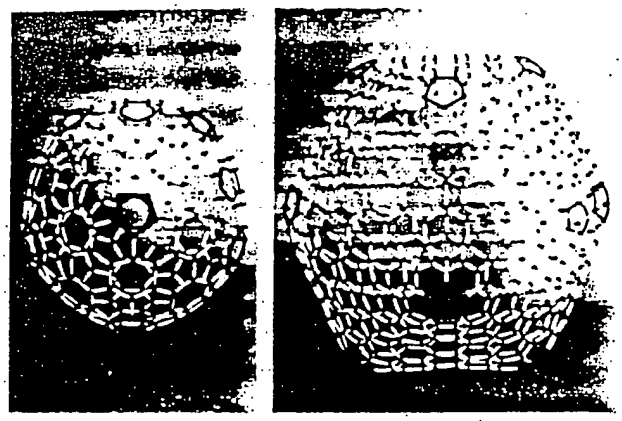

Fig. 18. Molecular models of the giant fullerenes C_{240} (left) and C_{540} (right). The models possess icosahedral shapes rather than perfectly spheroidal ones similar to the geodesic domes. Each of these structures can be considered as an initially flat hexagonal network which has warped into a closed monosurface (of icosahedral symmetry) by 12 pentagonal disclinations giving rise to the cusps.

that the giant fullerenes would be spherical like Buckminster Fuller's domes and had not looked carefully at Iijima's images. Even the most spheroidal giant fullerene (Fig. 19a) was clearly polyhedral (Fig. 19b). To see what one wants to see

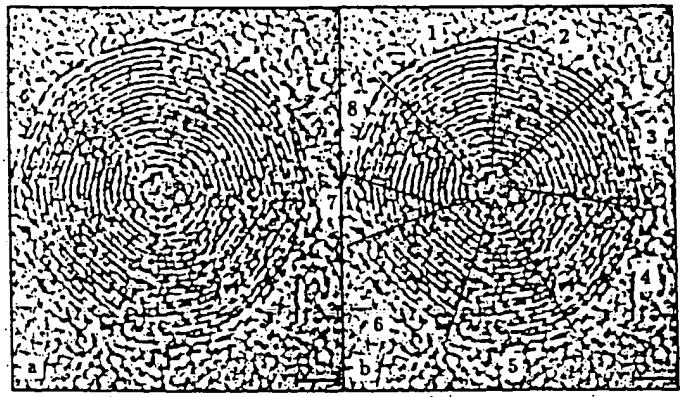

Fig. 19. The image obtained by electron microscopy of an onionlike graphite microparticle observed by Iijima [66] which appears superficially to be spheroidal (a). Careful scrutiny of this image, however, indicates that the object has a polygonal outline consistent with a set of concentric quasi-icosahedral fullerene-like shells (b) [65]. The marker indicates a scale of 20 Å.

rather than what is, is a cardinal sin for a scientist and the temptation is to be resisted at all costs.

The Quest for C_{60}

Until late 1989 the evidence in support of our structure proposal was, to my mind, very convincing, but it could not be deemed anything other than circumstantial. Clearly a macroscopic sample of C_{60} was needed—not just a whisper in a supersonic helium wind, detectable only by that ultrasensitive sensor, the mass spectrometer. At Sussex we sought more tangible evidence. The Science and Engineering Research Council (SERC) funded the construction of a cluster-beam apparatus, which was assembled with Tony Stace; Steve Wood helped us to obtain financial support from British Gas in the form of Collaborative Award in Science and Engineering (CASE) studentship for combustion-related studies. It was this assistance which was ultimately our salvation (vide infra). In a third project conducted with Ken McKay, we probed (by electron microscopy) the films produced by a carbon arc under helium in an old bell jar evaporator. We found that the film microstructure changed as the helium pressure was increased (to ca. 50 mmHg). The quadrupole mass spectrometer, with which I sought to monitor whether C_{60} was produced in this experiment, was the integral part of a modest carbon materials research project which failed to attract support from any funding source (including chemical companies). Because Stace and I had been quite generously funded by the SERC solely for the cluster-beam studies, another application (and indeed a rather applied one) to that source was difficult. Time slipped by and this program faltered even though I had put a great deal of effort into trying to obtain financial support.

The First Paper by Krätschmer, Fostiropoulos, and Huffman

In September 1989 Michael Jurá (UCLA Astronomy Department) sent me a copy of a thought-provoking paper[67] (Fig. 20) presented by Krätschmer, Fostiropoulos, and Huffman at a symposium on interstellar dust. This research group from Heidelberg and Tucson had observed four weak but distinct infrared absorptions in a film of arc-processed graphite, which were tantalizingly consistent with the expected spectrum of buckminsterfullerene. From theoretical studies[68] it was known that C_{60} should exhibit only four lines. What was more, the observed frequencies agreed quite well with those predicted. I had long followed the work of this group and knew that they had developed great expertise in studying carbon by spectroscopy. We had occasionally tried related studies, and I was only too aware of how tricky they were. I was sceptical about their result and also rather cha-

Harry - Presented at Capri -
Do you believe this? -H.

SEARCH FOR THE UV AND IR SPECTRA OF C_{60} IN LABORATORY-PRODUCED CARBON DUST

W.Krätschmer, K. Fostiropoulos *Max-Planck-Institut für Kernphysik, Heidelberg. W.-Germa*

and

D.R. Huffman *University of Arizona, Tucson, Arizona, USA*

Carbon dust samples were prepared by evaporating graphite in an atmosphere of an inert quenching gas (Ar or He). Changes of the spectral features of the carbon dust were observed when the pressure of the quenching gas was increased. At low pressures (order 10 torr), the spectra show the familiar broad continua. A high pressures (order 100 torr), narrow lines in the IR and two broad features in the UV emerge. The four strongest IR features are located in the vicinity of the lines predicted for the C_{60} molecule. One of the observed UV features may be related to the known 368 nm transition of C_{60}. It thus appears that at high quenching gas pressures C_{60} is produced along with the carbon dust.

Fig. 20. Annotated copy of the key paper presented by Krätschmer, Fostiropoulos, and Huffman at the conference *Dusty Objects in the Universe* in Capri (1989) [67]. This paper with the appended query was sent to me by Michael Jura (UCLA) who attended this conference.

grined. for had not Ken McKay and I made soot in a bell jar in exactly the same way three years before during the project, which we were forced to abandon through lack of funds?

I decided to resurrect the old and decrepit bell jar and with Jonathan Hare (holder of the British Gas CASE graduate studentship) tried to reproduce the infrared features obtained by Krätschmer et al. Michael Jura's missive arrived around September 1989, just before the start of the Sussex academic year, a time when third year undergraduate projects are needed. It does not matter whether these projects yield results; they should imbue the student with the flavor and excitement of genuine research, that is, the experience of working in the dark, not—as all too often happens—the frantic scramble for results at all costs! I had often initiated the most speculative of projects in this way, and my experience had shown time and time again that important and exciting studies could often start from such inauspicious beginnings. It seemed perfect for Amit Sarkar's third-year project, and he joined Hare on this wildly speculative project. Fairly soon these students succeeded in obtaining the IR bands (Fig. 21), which, although always very weak and highly irreproducible, confirmed the observations of the group from Heidelberg and Tucson. The obsolete apparatus then promptly fell to pieces! After rebuilding it almost completely from scratch, Hare tried to repeat the earlier observations, but consistent results eluded him. Sometimes he obtained the characteristic spectral features, sometimes they disappeared for days or weeks at a time. In retrospect, I suspect that the original discovery of the IR features by Krätschmer et al. could have been made by few other groups. Hare carefully varied every experimental parameter he could think of and finally developed the expertise to produce films which exhibited the telltale infrared features consistently. He wrote to Krätschmer about his efforts and received an encouraging reply containing useful advice. This certainly helped, because it was quite difficult to make films amenable to analysis.

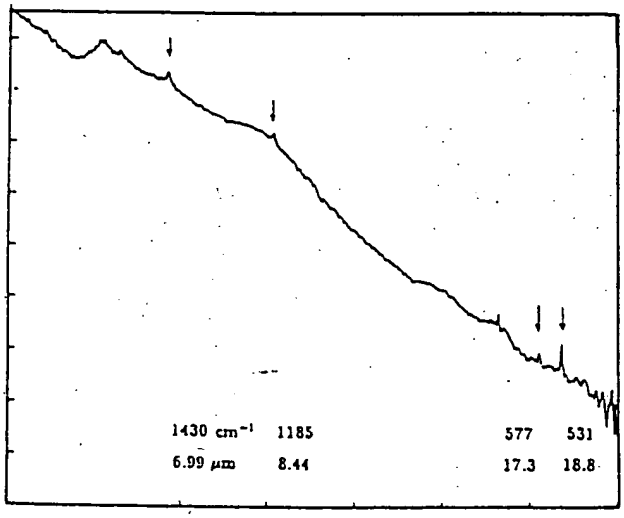

Fig. 21. Infrared spectrum of a film of arc-processed carbon obtained by Hare and Sarkar at Sussex which shows weak but clear (and confirmatory) evidence that the features first observed by Krätschmer et al. [67] (see Fig. 20) and tentatively assigned to C_{60} were real and repeatable.

The Dimerization of C_{30}

I spent about one month in the UCLA Astronomy Department around Easter 1990. One day, Mark Morris brought François Diederich from the Chemistry Department to see me. Diederich appeared excited and exhorted me to come to his office because he had something to show me. In response to his manner I somewhat disdainfully quipped, "You've not made C_{60}?" When he replied, "How do you know?", I was startled and suddenly became apprehensive since there was genuine surprise in his voice. When we arrived at his office he showed me an astonishing mass spectrum. In their attempts to make a pure carbon ring of 30 atoms Diederich, Rubin, Whetton, and their co-workers, had found that the molecule spontaneously dimerized to form C_{60} with almost unbelievable efficiency.[69] This staggering result seemed to answer, almost at a stroke, many puzzling questions that had been on my mind for years about carbon chains, their relationship with C_{60}, and soot. But I became even more apprehensive when I comprehended that the UCLA group might be on the verge of obtaining the coveted C_{60} NMR line. Subsequent discussions with David Walton, with whom I had probed aspects of the C_{60} formation mechanism,[70] alleviated my worries; he convinced me that scaling up the UCLA experiment so as to produce sufficient C_{60} for the key NMR measurement presented an enormous challenge.

Mass Spectrometry

I returned to Sussex and by early summer 1990 started to believe for the first time that C_{60} really might be in our sooty deposit. We therefore decided to probe the material by solid-state magic-angle-spinning (MAS) NMR. Indeed Ken Seddon (a Sussex colleague) had encouraged me to do this some years before. Perhaps the single ^{13}C NMR line was close at hand in the black soot, which at least we could now touch. I considered buying the most isotopically pure ^{13}C graphite, but that would have been very expensive, and we had no

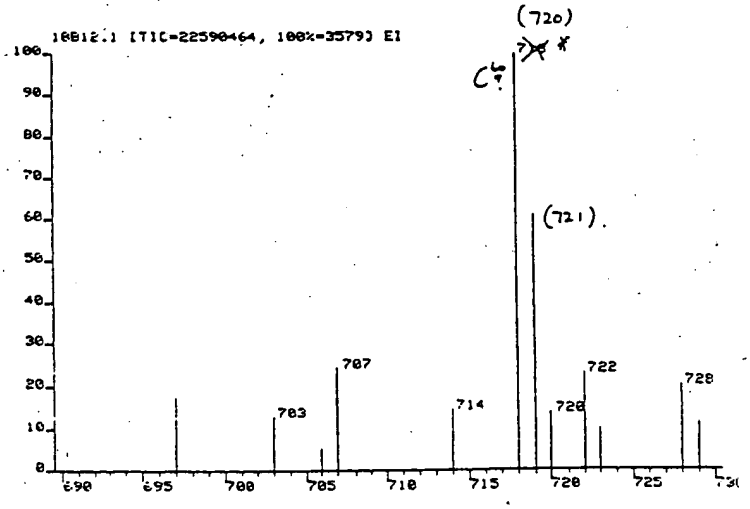

Fig. 22. Part of the FAB mass spectrum of a deposit of arc-processed soot obtained by Abdul-Sada on July 23rd, 1990 at Sussex. The calibration was off by 2 amu; however, the isotope pattern was convincing since the peaks are close to the intensity ratio 1.0:0.66:0.44 expected for $^{12}C_{60}$/$^{12}C_{59}$/$^{12}C_{58}$ $^{13}C_2$.

money anyway. The problem of generating enough material for solid-state NMR from the scrapings of thin sooty films, seemed insurmountable, especially since it was so difficult to produce the films in the first place, let alone analyze them. We really needed another way to monitor the samples, so we tried Fast Atom Bombardment (FAB) mass spectrometry. Ala'a Abdul-Sada helped us, and finally we obtained the mass spectrum shown in Figure 22. The signal containing the ^{13}C satellites was really quite convincing, but I wanted the result confirmed. The entry in Jonathan Hare's laboratory notebook on July 26th, 1990 (Fig. 23 top, second sentence) epitomizes many of our problems and requires little further comment.

The Red Solution

During this period we had considered the properties of C_{60}. What form would the compound take? Would it be a high-melting solid or a liquid? Would it be soluble? Benzene was an obvious solvent since C_{60} should look like benzene from every side (or at least from 20 sides). I remembered the little pink (or yellow) vial of liquid we used to talk about and wondered if the compound might even be volatile. In addition I had often discussed (with Smalley, Rohlfing, and others) how much C_{60} was being made in our experiments. The rough proportion which always seemed to arise was < 1 in 10000 of the total amount of carbon. At this level, given the amount of soot available, only a supreme optimist would attempt solvent extraction. Fortunately Hare is one—perhaps partly because he is a physicist working among chemists. On Friday, August 3rd Hare made up a mixture of the soot and benzene in a small vial, which he set aside over the weekend (Fig. 23, second entry). When he came in on Monday morning (August 6th) he noted (Fig. 23, third entry) that the solution looked "slightly red(d)ish" (Fig. 24). The generation of a red solution from pure carbon was scarcely believable. Hare made more material during the next few days and attempted mass spectrometric measurements on extracted material for the first time on Thursday, August 9th (Fig. 23, fourth entry).

possible use of FAB Mass Spect. 26/7/90.

Came back from Scotland Walk to find Fab Mass Spec had been done with exciting results. unfortunately the machine has been down so we can't repeat.

Results so far.

Seen - decent signal θ ($^{12}C_6$) = 720 amu !

also ^{13}C is ~1% of natural carbon so calculating shows that for C_{60} we should have 0.6% and have 0.5%

3/8/90

1) Made spot ½ a (30ml) tube of C_{60}^{6} + Carbon Powder, Actual Volume would be much smaller than this blue powder is so uncompact.

2) added about 25ml of Benzene and shook mixture

3) allowed to stand for Weekend.

6/8/90

Solution looks slightly reddish, tried to pipet liquid off from top but mixed up.

9/8/90

Volume lined sample to about 5th of volume could go lower (ie more concentrated) but we need about this Volume if we want to use IR liquid cell, so will keep to this.

(Continued evaporation down to about 4-5 drops (but ?). FAB showed No C_{60} (720).

Fig. 23. Entries by Hare in his laboratory notebook: July 26th, 1990; August 3rd, 1990; August 6th, 1990; August 9th, 1990.

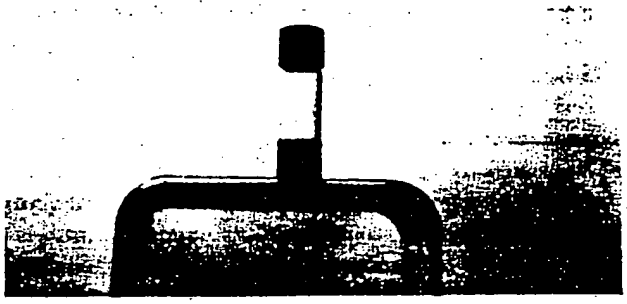

Fig. 24. Original reddish extract obtained on Monday, September 6th, 1990 (see Fig. 23).

About 10 o'clock the next morning (Friday, August 10th) I received a telephone request from the journal *Nature* to referee a paper by the Heidelberg/Tucson group which I accepted. I was totally unprepared for the bombshell which arrived minutes later by telefax. Following up their own earlier work, Krätschmer, Lamb, Fostiropoulos, and Huffman had successfully sublimed from their carbon deposit a volatile brown material, which dissolved in benzene to give a RED SOLUTION (!!!!!).[71] Crystals obtained from this solution yielded X-ray and electron-diffraction data commensurate with material composed of arrays of spheroidal molecules 7 Å in diameter separated by 3 Å, just as expected for buckminsterfullerene. This beautiful paper even contained photographs of crystals. I was convinced that they had isolated C_{60}, and we had been pipped at the post. Somewhat stunned, I pondered our demise and faxed my report back to *Nature* after lunch. I recommended that the paper be published without delay and requested the editor to convey my sincere congratulations to Krätschmer and his associates.

This was what the British call a difficult moment, but as I slowly surveyed the damage I realized that all was not quite lost. It gradually dawned on me that there was not a single(!) NMR line to be seen in the manuscript (nor was there a mass spectrum. We later learned that they had the mass spectrum, but certain problems had arisen which precluded its inclu-

sion in the manuscript.) At this point we had spent nearly a year struggling independently learning how to make the arc-processed material: we had made our own soot, we had confirmed the presence of C_{60} mass spectrometrically, and we had solvent-extracted the red material—and all this *before* the manuscript arrived. I decided that we were not going to abandon our efforts now after we had achieved all this. We still had a lot going for us, and I thought we might be able to obtain the desired NMR result. However, now that the Heidelberg/Tucson study was essentially in the public domain it would be transmitted around the world by telefax within hours. I had studiously tried to avoid such situations in science—competition—all my life: my philosophy is to probe areas in which few others, preferably no one, work. That is where, it seems to me, the most unexpected discoveries are likely to be made.

We had to act very quickly if five years of effort were not to be completely in vain. A race must be on because the material was now so easy to make, and it could not be long before other groups, far better equipped than we, recognized that there was one last exquisite prize remaining in the story of the discovery of C_{60}—the NMR line. Our one priceless advantage was that Hare had already made a reasonable quantity of material, and that, at that moment, only the Heidelberg/Tucson group had any at all. We needed help and fast. Roger Taylor, an organic chemist, provided the desperately needed expertise: he separated the material quickly and efficiently. Since our mass spectrometer had broken down again, Hare rushed by train to Manchester with a sample of the precious extract. Numerous frantic telephone calls passed between Sussex and Manchester, because the sample refused to respond to analysis. Then with a key piece of advice from Taylor about solubility, the Manchester operators (at Kratos) managed to dissolve the material in the FAB matrix and obtained the FABulous mass spectrum shown in Figure 25. It was hard to believe, but besides C_{60} other fullerenes with 56 to 72 atoms were detected: in particular, C_{70} was abundant. The whole family of fullerenes appeared to be present in the soot, not just C_{60}!

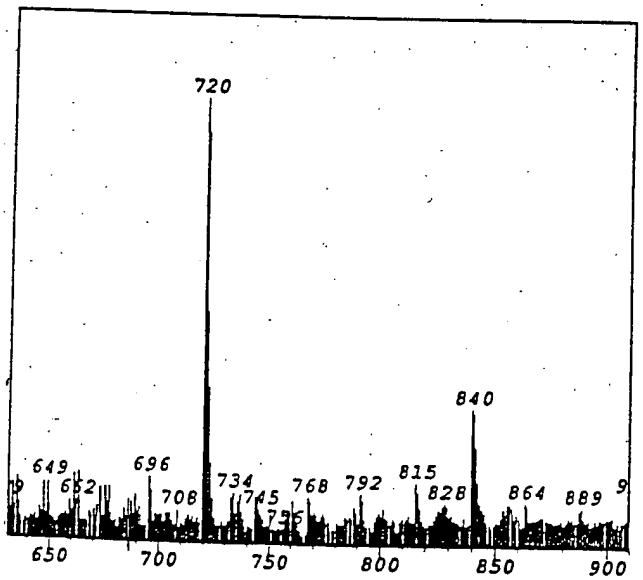

Fig. 25. Part of the FAB mass spectrum of the red extract which confirmed that it consisted mainly of C_{60} and C_{70}. The spectrum also indicates the presence of other fullerenes [72].

C_{60} is Magenta (Pink?) in Solution

Taylor noted that the extract was soluble in hexane and recognized that he might be able to separate the fullerenes chromatographically. To his delight he found that on an alumina column resolution into two bands, one red, the other magenta, could be achieved. The magenta fraction, (Fig. 26) was a delight to the eye in the delicacy of its color.

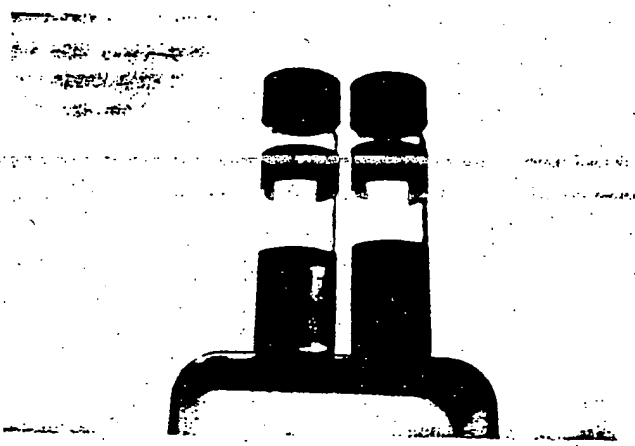

Fig. 26. Chromatographic separation of the red extract by Taylor resulted in a magenta C_{60} fraction (left) and a red C_{70} fraction (right).

Its mass spectrum showed a peak at 720 amu, and we sent the sample to Tony Avent for NMR analysis. We were summoned to see our single line (Fig. 27), which Avent assured

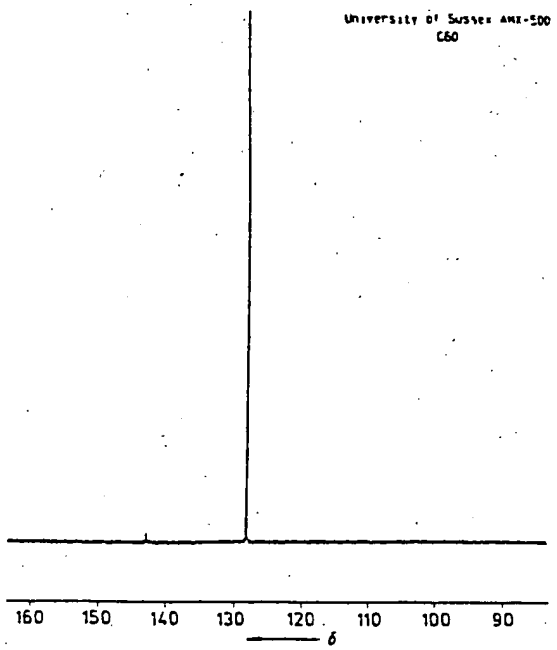

Fig. 27. The first NMR spectrum in which the C_{60} resonance (at $\delta = 143$ ppm) was first identified (barely). The strong line at $\delta = 128$ ppm is (rather appropriately) the resonance of benzene.

us was present. So this was it: a line so small I needed a microscope to see it! Could this insignificant little blip really be the line I had dreamed about for five years? Further work confirmed beautifully that this was the result which we had sought for so long.[72] The joy alleviated almost all the despair I had first felt on reading the paper by Krätschmer et al. One might have thought, as some said, that I should have been pleased to have been proven right when so many had been sceptical. That was not my feeling, probably because I had known ever since the recognition of C_{70} as the second magic fullerene[51] that our structure could not possibly be wrong. I know that my colleagues at Rice University also had no doubts.

What about C_{70}? It turned out to be the icing on the cake, although not without attendent trauma. The wine-red fraction which had masked the pale magenta of C_{60} yielded a mass spectral peak at 840 amu and was clearly C_{70}. According to the expected structure (Fig. 15 right) this compound should exhibit a ^{13}C NMR spectrum with five lines. On Sunday, September 2nd, 1990 I entered the laboratory at the same time as Avent who told me the C_{70} measurement should have just been completed. The spectrum we plotted was sensational—or almost so. There were indeed five lines, but one was in the same position as the C_{60} peak. Could it be that one line was underneath the C_{60} signal? After repeated chromatography to remove the last vestiges of C_{60}, further NMR studies showed the fifth line to be rather different from the others. The resonance of the ten atoms in the waist (Fig. 28c) is more "benzenoid" than the other four resonances.[72] Indeed this line lies dangerously close to the benzene solvent line: had it been a little closer to the benzene signal it would have been swamped and missed altogether. In many ways the five lines of C_{70} are (arguably) more important and significant than the C_{60} singlet. For one thing, they confirm that fullerene carbon atoms are not fluxional; for another, they show that the atoms are not on the perimeter of a monocyclic ring. Both of these cases would lead to a spectrum with a single resonance. Even more important was the fact that the NMR results confirmed the family concept for fullerene cages. It was now clear that a host of stable fullerenes were just waiting to be discovered, as we had long suspected.[53]

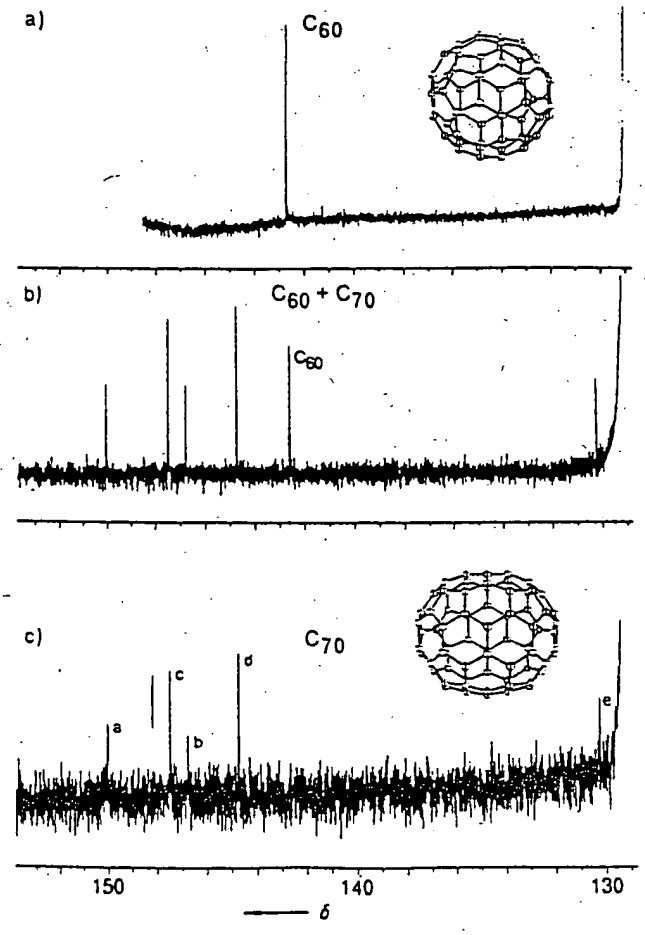

Fig. 28. ^{13}C NMR spectra obtained from chromatographed samples of soluble material extracted from arc-processed graphite: a) spectrum of purified C_{60} (magenta fraction); b) mixed C_{60}/C_{70} sample; c) spectrum of purified C_{70} (red fraction) showing five lines as expected for the symmetric egg-shaped molecule (see Fig. 15).

"The Third Man" is as Elusive as Ever in Space

The elusiveness of C_{60} and my belief that it has been lurking in that blackest of black materials, soot, since time immemorial often reminded me of the role played by Orson Welles in the film "The Third Man". The spirit of this antihero pervades the whole movie although he is seldom seen. Indeed he makes his first appearance late on in the movie in the black shadows of a dark street in Vienna when his face is suddenly illuminated by a light being switched on. For five years C_{60} played a very similar shadowy role—at least as far as I was concerned. My part in the buckminsterfullerene story really started out in space, and this celestial sphere has come down to earth with more of a bounce than a bump; but will it bound back up into space? Is this third form of carbon distributed ubiquitously in space as we surmised the day we found it in the laboratory?[41] Now that we know something about fullerene-60, we should be able to study all its optical properties. It is clear that the UV radiation density in the optically observable interstellar medium is such that the species will be ionized.[73] The possible existence of encapsulated complex ions[73, 74] is quite interesting. However, even with buckminsterfullerene in our hands, we find that this "third man" is as elusive as he ever was in the space between the stars. Perhaps the interstellar form is related to protonated carbon monoxide (HCO^+), which Bill Klemperer identified about 20 years ago.[17] If there are any C_{60} molecules in space there can be little doubt that most will have a proton or some other atom adhering to their surface.[74] $C_{60}H^+$ could probably survive for eons. Other abundant elements, particularly alkali and alkaline-earth metals, must also stick to the surface. Such species will have fascinating optical spectra. For instance, the energy and wavelength of the charge-transfer transition $(C_{60}^+)X \rightarrow (C_{60})X^+$ can be estimated to a first approximation as simply the difference between the ionization potentials of the separated species. For $(C_{60}H)^+$ this transition lies at about 2200 Å. For $(C_{60}Na)^+$ and $(C_{60}K)^+$ the transitions lie in the region of the Diffuse Interstellar Bands[33] and for $(C_{60}Mg)^+$ near zero frequency(!) These observations imply that this and related species will have unusual electrical properties. These processes are probably related to the recently observed superconductivity

of metal-doped fullerene-60 materials.[75] This conjecture is supported by an important new result which comes not from work with bulk material but from cluster-beam studies by McElvaney and Callahan.[76] They found that the gas-phase proton affinity of C_{60} is similar to that of ammonia—a remarkable result! I like to put my trust in intuition: when all else fails it is, after all, our only guide: It is curious to note that some important spectral features of space (the Diffuse Bands) have been visible for decades, yet we do not know what causes them. Now we have discovered that an unexpected molecule, C_{60}, has been under our noses on earth since time immemorial and was invisible until now. It seems to me highly likely that these two observations will turn out to be connected.

Epilogue

Since the time that graphite balloons and C_{60} were twinkles in the eyes of David Jones, Eiji Osawa, and a few other imaginative scientists,[42, 43, 46–48] there have been many significant contributions, both experimental and theoretical, to the first chapter of the buckminsterfullerene story which has just been completed. These have recently been comprehensively reviewed.[77] Figure 12 shows the Rice/Sussex team and Figure 29, the Sussex Buckaneers. These two teams together with the Heidelberg/Tucson team scored many of the goals in the football match which has just ended. Many new teams have now started to play an exciting, but different, ball game. The important difference is that the players can now see what they are kicking.

Fig. 29. The Sussex Buckaneers football team: From left: Kroto, Abdul-Sada, Taylor, Hare, and Walton.

Apart from the successful observation of the "lone" NMR line, two other matters give me a sense of deep pleasure: one was the beautiful color of C_{60} and, furthermore, that it was seen first at Sussex. The second was that apparently no one else appeared to have followed up the early IR results obtained by the group from Heidelberg and Tucson (September 1989). In retrospect I find this astounding; perhaps it was because the work appeared in the astronomy literature, but more likely it was because research today is carried out under such pressure, and our fear of failure is so great (and exacerbated by funding procedures). Few groups enjoy the luxury of working in the dark—a condition which I feel lies at the heart of true scientific endeavor. I have a videotape of a marvellous BBC documentary on Richard Feynman (the greatest lecturer I had ever heard) from the series "Horizon". In one part he talks on essentially this topic. This 50 minute program had the most profound effect on me. At one point Feynmann described how, when he was hired at Cornell, Bob Wilson had told him that it was the university's responsibility whether he accomplished anything—it was their risk(!) It was not for Feynman to worry about, he should amuse himself. In this way he was freed from the psychological burden of doing anything "important", and he was able to relax and do what he most enjoyed—physics and mathematics—just for the fun of it. How lucky he was. I know of few professional scientists today, certainly no young ones, who are in such a utopian scientific environment. What a sad reflection on today's research, especially since we know in our hearts that human beings achieve most when they are free of pressure. We know that small children learn and discover the joys of nature most efficiently during their play.

News of the breakthroughs spread like wildfire during September 1990, and the method of production developed by the Heidelberg/Tucson group was immediately improved upon[78] at Rice University. As soon as it was known that fullerenes are chromatographically separable and that solution NMR is feasible, other groups confirmed these measurements.[79, 80] Don Huffman remarked laconically at a recent symposium, "Everyone is able to repeat these experiments".

A new postbuckminsterfullerene world of round organic chemistry and materials science has been discovered overnight. Almost every day a new paper appears on some novel aspect of fullerene behavior. The group from Rice University has shown that C_{60} forms species such as $C_{60}H_{36}$.[78] Hawkins et al. have made an osmium complex in which the spinning of the fullerene ball is stopped and has enabled accurate bond lengths to be determined.[81] NMR studies by Yannoni et al. have also yielded accurate bond lengths.[82] The radical anion has been polymethylated by Olah's group;[83] platinum complexes have been prepared at DuPont.[84] At AT&T it has been found that the metal-doped material now holds the temperature record for molecular superconductivity.[75] Fascinating differences in the crystal structure of C_{60} have been found which depend upon how the crystals are produced.[77] Foote and co-workers at UCLA have shown that C_{60} transfers light energy efficiently to generate singlet oxygen.[85] Diederich, Whetten, and co-workers have evidence for oxides such as $C_{70}O$.[86] C_{60} is decomposed by light under circumstances which still need to be fully identified.[87] Also interesting is the fact that more fullerenes, such as C_{76} and C_{84}, are being extracted and characterized.[86] The fullerene family has arrived in force, and there are balls of all shapes and sizes for everyone to play with.

This advance is an achievement of fundamental science, not applied science, and serves as a timely reminder that fundamental science can achieve results of importance for strategic and applied areas. The origin of the whole program lay in an interest in aspects of molecular dynamics, allied

with the quest for an understanding of the origin of the carbon chains in space and their possible relationship to circumstellar and interstellar grains as well as soot.[11] These ideas welded together beautifully with the major advance in cluster science brought about by the experimental techniques developed by Smalley and co-workers at Rice University. Krätschmer and Huffman and co-workers were originally motivated by an interest in space dust and, in their recent breakthrough, by astrophysical implications of C_{60}. The C_{60} story has many facets, but more than anything else it is yet another archetypal lesson on the benefits to be gained by supporting pure fundamental science. The field has exploded, and its applications in chemistry and the science of materials are only just starting to be explored. Finally it is worth noting that C_{60} might have been detected 20–40 years ago, perhaps in a sooting flame; one wonders why it took so long.

Another lesson may be learned from these acknowledgements. Important contributions were made in research programs at the University of Sussex (Brighton, UK), the National Research Council (Ottawa, Canada), Rice University (Houston, Texas, USA), the Max-Planck-Institut für Kernphysik (Heidelberg, Germany) and the University of Arizona (Tucson, USA). The discovery of C_{60} is a tribute to not only the international nature of science but also the necessity of interdisciplinary cooperation. The contribution from the University of Sussex to the story started as a consequence of the "Chemistry by Thesis" degree course initiated by Colin Eaborn, which enabled undergraduates (such as Anthony Alexander) to carry out research with supervisors from more than one field. It could only have been successful in the interdisciplinary scientific research and teaching environment which the university pioneered when Sussex was founded in the "optimistic 60s". Sadly this and other courses have been "regulated" out of existence by bureaucrats who have little understanding of how student research expertise is brought to maturity and no awareness of the dire consequences for our future scientific capability. The first part the story could also not have been achieved had chemistry at Sussex been divided into those traditional subsections of organic, inorganic, and physical chemistry. I also had close contacts with astronomers at Sussex, particularly Bill McCrea and Robert Smith. The carbon discoveries resulted from a free-wheeling research program which started with synthetic chemistry (with David Walton, Anthony Alexander, and Colin Kirby) and moved via spectroscopy and quantum mechanics to radioastronomy (with Takeshi Oka, Lorne Avery, Norm Broten, and John MacLeod at the NRC). It moved back to the laboratory and chemical physics (with Jim Heath, Sean O'Brien, Bob Curl, and Rick Smalley at Rice University). In the last phase, key advice came from Michael Jura (an astronomer) which initiated some basic chemistry (with Jonathan Hare, Amit Sarkar, Ala'a Abdul Sada, Roger Taylor, and David Walton). Apart from those mentioned in the text who played direct (and sometimes crucial parts) such as Steve Wood of British Gas, I also acknowledge greatly the help of many others who played indirect parts, particularly graduate students and post-doctoral fellows as well as colleagues such as Tony Stace, Roger Suffolk, and Mike Lappert. Finally I wish to thank Ed Wasserman for some invaluable advice and David Walton in particular for his unfailing help throughout the period of this story and his painstaking assistance in preparing this account.

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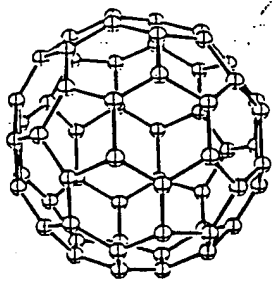
The cover picture shows a section of a high-frequency oven used in a novel synthesis of fullerenes. The reaction zone (at approximately 2800 °C, the light is dimmed by the soot beginning to deposit) is depicted at the start of the fullerene production. The inductor, boron nitride insulation tube, quartz tube, and initial formation of smoke can be seen. More about the novel efficient synthetic method is reported by M. Jansen and G. Peters on page 223. The boom in fullerene chemistry continues. The third in a series of highlights on the important recent results (previous updates were published last year in the January and June issues) will appear in the next issue. An overview of the preparations, properties, and reactions of C_{60} is planned. This issue includes two highlights on silicon clusters including Si_{60} (p. 173), a communication on $He@C_{60}$ (p. 183), and, last but not least, an exciting account by H. Kroto on the start of the fullerene story (p. 111).

Review Articles

A "round organic chemistry" has burgeoned this last year following the development of an efficient means of producing fullerenes in 1989/1990. One of the protoganists in the fullerene story describes in a lively personal style how this fascinating new chemistry came about. In this thriller he points out that the discovery of C_{60} in 1985 did not result from an applications-oriented search but rather from basic research and scientific curiosity.



C_{60}

H. W. Kroto*

Angew. Chem. Int. Ed. Engl. 1992, *31*, 111...129

C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

Almost atomic resolution is achieved today in techniques for studying monomolecular Langmuir films of amphiphilic molecules. Synchrotron X-ray sources providing well-collimated, high-intensity radiation make this possible. In this review the principles and methods used to study thin films are discussed. In these investigations, for instance, a strong influence from solute molecules or ions in the subphase on the crystallinity of the monomolecular layer was revealed: whereas α-glycine increases the crystallinity of a fluorocarbon monolayer, β-alanine decreases it. Possible explanations for the phenomena are also presented.

D. Jacquemain, S. G. Wolf, F. Leveiller, M. Deutsch, K. Kjaer,* J. Als-Nielsen,* M. Lahav,* L. Leiserowitz*

Angew. Chem. Int. Ed. Engl. 1992, *31*, 130...152

Two-Dimensional Crystallography of Amphiphilic Molecules at the Air–Water Interface

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C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

By Harold W. Kroto*

In 1975–1978 the long-chained polyynylcyanides, HC_5N, HC_7N, and HC_9N were surprisingly discovered in the cold dark clouds of interstellar space by radioastronomy. The subsequent quest for their source indicated that they were being blown out of red giant, carbon stars. In 1985 carbon-cluster experiments aimed at simulating the chemistry in such stars confirmed these objects as likely sources. During these cluster studies a serendipitous discovery was made; a stable pure-carbon species, C_{60}, formed spontaneously in a chaotic plasma produced by a laser focused on a graphite target. A closed spheroidal cage structure was proposed for this molecule, which was to become the third well-characterized allotrope of carbon and was named buckminsterfullerene. It has taken five years to produce sufficient material to prove the correctness of this conjecture. There may be a timely object lesson in the fact that exciting new and strategically important fields of chemistry and materials science have been discovered overnight due to fundamental research, much of which was unable to attract financial support, and all of which was stimulated by a fascination with the role of carbon in space and stars. In this account, interesting aspects of this discovery, its origins, and its sequel are presented. The story has many facets, some of which relate to the way scientific discoveries are made.

Molecules with Unsaturated Carbon Bonds

In the early 1970s, the chemistry of carbon in unsaturated configurations became the prime research focus for my group at the University of Sussex.[1] We were interested in free unstable species and reaction intermediates containing C-S, C-P, C-Si, or even C-C multiple bonds. The work originated from an abortive attempt to produce thioformaldehyde ($H_2C=S$) by photolysis. However, we switched immediately to thermolytic activation after I heard a lecture in which Don Johnson (from the U.S. National Bureau of Standards in Washington, D.C.) described how he and Powell had made this compound[2] by passing MeSSMe vapor through a quartz tube heated simply by a bunsen burner! This approach worked beautifully; we produced numerous other new compounds containing the C=S moiety such as thioethanal and thioketene by thermolysis of specially synthesised precursors, and characterized them mainly by microwave and photoelectron spectroscopy.[1] These sulfur species possessed a distinctive odor, and I for one have sympathy with the citizens of Freiburg who, according to Noller,[3] forced Baumann and Fromm to abandon their work on these compounds. We gave up our work on seleno analogues for similar reasons after detecting selenopropanal! After success with sulfur/carbon compounds we jumped, in the spirit of Mendeleev, to the next element in the second row of the periodic table, phosphorus. The first phosphaalkenes, $CH_2=PH$ and $CH_2=PCl$,[4] were produced in 1976 in a joint project with John Nixon; several more followed.[1] Simultaneously, Becker in Germany made $PhP=C(tBu)OSiMe_3$.[5] At this stage I envisaged a simple possible solution to the problem which had been on my mind

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since 1964, namely to ascertain whether derivatives of Gier's beautiful molecule HC≡P[6] could be made. I had been fascinated with HC≡P since the day I arrived as a postdoc at the National Research Council (NRC) laboratory in Ottawa and heard Takeshi Oka (who was then also an NRC postdoc) enthuse over a spectrum of this molecule which Kelvin Tyler (another NRC postdoc) had just obtained.[7] It seemed to me that the chemistry of HC≡P and its analogues must parallel that of the nitriles. Transition-metal complexes could probably be prepared, and cycloadditions to generate phosphorus-containing rings would be feasible.[8, 9] The simple approach worked very well, and we produced the first phosphaacetylene derivative, $CH_3C{\equiv}P$,[10] by thermolysis of $EtPCl_2$ (provided by R. Schmutzler). We followed this breakthrough with the syntheses of other XC≡P species (X = Hal, Ph, N≡C, N≡C−C≡C, etc.[11]). It is most satisfying that, as I had originally conjectured in 1964, the phosphaalkynes (and the phosphaalkenes) have subsequently been exploited by ourselves and other groups as synthetic building blocks.

In parallel with our studies of compounds made up of second-row elements and carbon we probed molecules containing chains with C−C multiple bonds. My fascination with such chains developed very early on in a study of the peculiar molecule, carbon suboxide O=C=C=C=O (one subject of my Ph.D. work at Sheffield in the early 1960s with my supervisor Richard Dixon). This stimulated my curiosity in extended carbon chains and the unusual flexibility which they often exhibited; a preoccupation with such molecules has continued to this day. When I flash-photolyzed C_3O_2 a year or two later at the NRC, I ended up with a cell full of black soot and a magnificent spectrum of the C_3 molecule, whose enigmatic patterns had finally been deciphered by Gausset et al.[11] Almost everything about these carbon chains seemed idiosyncratic, and I stored such observations up for the future. These memories were reawakened in the early 1970s by David Walton's work on polyynes at the University of Sussex. David had developed elegant methods for synthesizing long-chain polyynes, based upon silyl-protection techniques which he pioneered in acetylene chemistry.[12–14] He and his students had made the parent 24 carbon-atom species in minute quantities in solution and

H−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−H

even a 32 carbon-atom (silyl-protected) polyyne.[13] These chains were precisely what was needed for a study of vibration–rotation dynamics—a topic which had attracted my interest. In my mind they conjured up an image of a microscopic quantum-mechanical cheerleader tossing a very bendy bamboo baton high into the air—and then attempting to catch the violently flexing and turning baton it as it descended. The obvious first compound for microwave study was the cyanopolyyne, HC_5N, because of its expected enormous dipole moment. Walton devised a synthetic route; Anthony Alexander, a "Chemistry by Thesis" student (editorial comment: for an explanation see the acknowledgements at the end of the review), successfully prepared it and measured its microwave spectrum in 1974.[15] This was a wonderful achievement for an undergraduate and a very important one for me, since it was the first molecule to be characterized on our newly acquired microwave spectrometer.

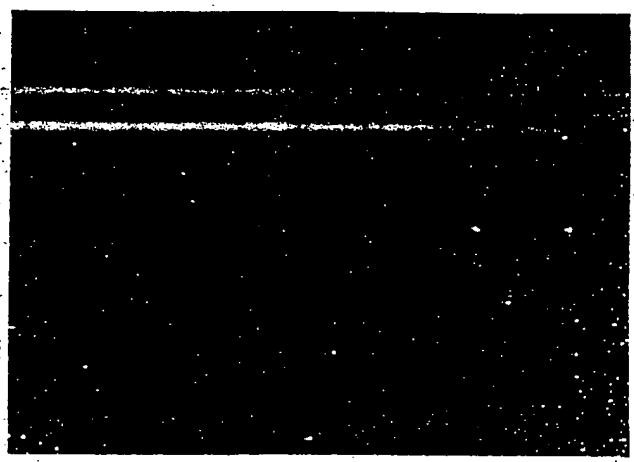

Fig. 1. The dark clouds in Taurus from Barnards 1927 survey. *Atlas of Selected Regions of the Milky Way*, (Ed.: E. B. Frost, R. Calvert), Carnegie Institute, Washington, D.C., 1927. Heiles's Cloud 2 is in the left-hand bottom corner as indicated by coordinate markers.

At about this time spectacular advances were being made in molecular radioastronomy. The black clouds which are smeared across our Milky Way galaxy (Fig. 1) were found to possess long-hidden dark secrets. Townes and co-workers[16] opened the Pandora's box in 1968 and revealed that the clouds are full of identifiable molecules. Astronomers suddenly realized what a key role molecules played in the

Harold Kroto, born in 1939, studied in Sheffield from 1958 to 1964 and received his Ph.D. for his research in the electronic spectroscopy of free radicals with R. N. Dixon. After three years of postdoctoral research at the National Research Council in Ottawa and Bell Laboratories, he started his academic career in 1967 at the University of Sussex in Brighton, where he became full professor in 1985. The most recent distinction Kroto has received is a Royal Society Research Professorship (1991). Since 1990 he has been chairman of the editorial board of the Chemical Society Reviews. His research interests include the spectroscopy of unstable species, carbon and metal clusters and microparticles, as well as interstellar molecules and circumstellar dust. Graphic design is his other passion.

intimate gas dynamics involved in the birth of stars and planets. Apart from well-known species such as ammonia, water, and ethanol—enough for 10^{28} bottles of schnapps in Orion alone—Bill Klemperer ingeniously identified the HCO^+ ion (protonated CO)[17] which had not previously been detected in the laboratory. Thus space served not only as a playground reserved for astronomers, but it now presented chemists with a novel piece of apparatus, indeed a colossal new spectroscopic sample cell, containing a plethora of exotic molecules in a wide range of physico–chemical environments.[18] Shortly after Turner[19] had detected HC_3N by microwave frequencies, I wrote to Takeshi Oka at the NRC; my group had recorded the analogous frequencies of HC_5N, and I wanted to search for the molecule in space. Takeshi and I had worked (1964–1966) in the same laboratory at the NRC during the golden years of that research organization.[*] He replied saying that he was "very, very, very, very, very much interested".

In November 1975 the search for radio waves of HC_5N (with Canadian astronomers Lorne Avery, Norm Broten, and John MacLeod) resulted in the successful detection of a signal from Sgr B_2, a giant cloud of molecules near the center of the galaxy.[20] Although we had been hopeful, we were surprised by our discovery since it had seemed such a long shot. In 1975 molecules with more than three or four heavy (C, N, or O) atoms were assumed to be far too rare to be detectable. However, having found HC_5N in space, we thought that HC_7N might also be present. Walton devised a synthesis of HC_7N, and graduate student Colin Kirby managed the very difficult problem of making it and measuring its spectrum.[21] By the time Colin (in England) finally succeeded in recording the vital frequency, we were actually working on the radio telescope, since our allotted observing session had already started. Colin telephoned my wife, who wrote the value on an envelope (Fig. 2 left). She then telephoned Fokke Creutzberg, a friend in Ottawa, who also noted it carefully (Fig. 2 right) and transmitted it to us at the telescope site in Algonquin park (Fig. 3). The next few hours were high drama. We dashed out to the telescope and tuned the receiver to the predicted frequency range as Taurus

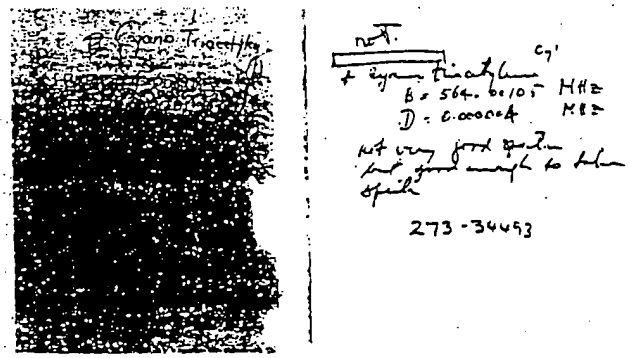

Fig. 2. The envelope (left) and intermediate note (right) with the precious experimental data from which the frequency of HC_7N in space was determined.

[*] Under the guidance of Gerhard Herzberg the NRC had become the Mecca for spectroscopists, and it was here that Cec Costain introduced me to the delights of microwave spectroscopy.

Fig. 3. The 46 m radiotelescope in Algonquin Park, Ontario, Canada with which the long-chain carbon molecules in space were detected.

(Fig. 1) rose above the horizon (perfect timing). We tracked the extremely weak signals from the cold dark cloud throughout the evening. The computer drove the telescope and stored incoming data, but to our frustration we could not process the data on-line while the telescope was running. The system did, however, display individual ten-minute integrations, and as the run progressed we watched the oscilloscope for the slightest trace of the predicted signal in the receiver's central channel. During the course of these ten-minute snapshots, we gradually concluded that the central channel signal was possibly higher on the average than nearby ones. Desperate for even the faintest scent of success, we carried out a simple statistical analysis in order to determine whether the signal level of the channel was greater than the noise. As the night wore on we became more and more excited, convinced that the signal was significantly more often high than low; we could hardly wait for Taurus to set. By 1:00 a.m. we were too excited and impatient to wait any longer, and shortly before the cloud vanished completely, Avery stopped the run and processed the data. The moment when the trace in Figure 4 appeared on the oscilloscope was one of those that scientists dream about and which, at a stroke, compensate for all the hard work and the disappointments which are endemic in life. The circumstances of this discovery—the arrival of the value of the microwave fre-

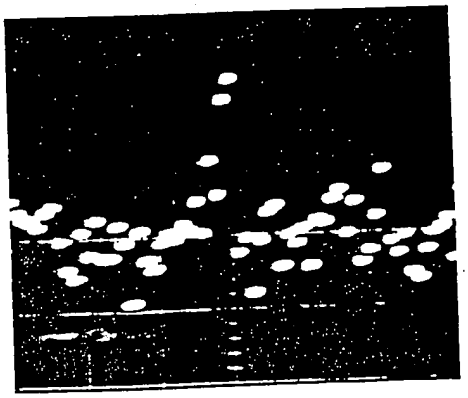

Fig. 4. The first oscilloscope trace of the radio signal emitted by interstellar HC_7N in Heiles's Cloud 2 in the constellation of Taurus (see the coordination markers in Fig. 1).

quency from the UK just in the nick of time, the gradual growth of the conviction that there might be a signal in that central channel of the receiver, and then finally the revelation that we (Fig. 5) had detected an enormous molecule in space[22]—made for a truly cathartic scientific experience. (Modern on-line data processing would have diminished the experience). Obviously, the next candidate was HC_9N, but

Fig. 5. The team at the NRC laboratory just after the detection of HC_9N in space (from left): Avery, Oka, Broten, MacLeod, and Kroto.

its synthesis was a daunting task. Fortunately, Oka developed a beautifully simple extrapolation technique with which he predicted the radio frequencies of HC_9N. Almost unbelievably, we detected this molecule as well![23] Bell et al. later detected even $HC_{11}N$.[24]

The Search for the Source of Carbon Chains in Space

It is not so obvious today, but in 1975–1978 such long-chain molecules were a totally new and unexpected component of the interstellar medium. How such species came to be present was not at all clear. I felt that it was not sufficient just to have co-discovered them; I really wanted to solve the puzzle of how they got there in the first place, and indeed what they were doing there anyway. After all, everything in nature seems to have some role to play. The search for the source of these compounds became something of a preoccupation (even an obsession). By the early 1980s I was convinced that the ion–molecule reactions which Eric Herbst and Bill Klemperer,[25] and Alex Dalgarno and John Black[26] had devised, and which accounted beautifully for almost all other interstellar molecules, really could not explain the origins of chain molecules.[1, 18] It gradually became clear to me that red giant, carbon stars must hold the key. Particularly interesting was the spectacular infrared object IRC+10216, discovered by Eric Becklin and his colleagues,[27] which pumps vast quantities of chains and grains out into space. I wondered about this red giant and the fact that it was shrouded in grains and chains, which were formed at roughly the same time,[1, 18] and whether "the long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2, and C_3, which are well known, and particles with high carbon content such as soot".[1] Perhaps some symbiotic chain/dust chemistry was involved.

The First Visit to Rice University (Easter 1984)

The foregoing account sets out the background for my thoughts about the role of carbon in space prior to my trip to Rice University in Texas during Easter 1984 to visit Bob Curl. Almost the first thing that Curl told me was that I should visit his colleague, Rick Smalley. He enthused over a very recent result obtained by Smalley and his co-workers, who had analyzed the spectrum of the SiC_2 and had shown the molecule not to be linear, as some might have expected, but triangular.[28] (The analogous C_3 species is linear, although only just.[11]) I visited Smalley's laboratory and saw the laser vaporization cluster-beam apparatus which he and his co-workers had recently developed. This powerful technique enabled the mass-spectrometric study of stable clusters formed in a helium-entrained plasma, produced by a pulsed laser focused on a solid target. In this particular experiment silicon carbide was vaporized and the electronic spectrum of SiC_2 observed.[28] I was much impressed by the result but even more by the experimental technique.[29] This method was clearly a major breakthrough in cluster science, since it made refractory clusters accessible for detailed study for the first time. I had already heard of it, but to see the apparatus in operation was quite fascinating. The result of the SiC_2 experiment was particularly interesting to me, because it was consistent with some unusual theoretical results for >Si=C< species[30] obtained at Sussex in collaboration with John Murrell some years earlier. What excited me most, however, was the thought that by simply replacing silicon carbide with graphite, it should be possible to simulate the type of chemistry which takes place in the atmosphere of a carbon star and produce the long carbon chains. As the day wore on I became more and more convinced that the technique was perfect for this purpose and that evening discussed it with Curl. Because of his interest in microwave spectroscopy, he was immediately enthusiastic, and we made plans for a joint project in the hope that Smalley would also be interested. Perhaps we could detect chains with as many as 24–32 carbon atoms related to Walton's polyynes or Hintenberger's equally amazing pure-carbon species (C_{33} etc.), which were detected by mass spectrometry in the early 1960s in a carbon arc.[31] I dreamt that one day it might be possible to detect a chain molecule such as $HC_{33}N$ (which is as long as the chains that Walton had made in a test tube) in space. Curl was particularly excited by the prospect that we could check out an interesting idea of the late Alec Douglas,[32] namely, that carbon chains might be carriers of the famous Diffuse Interstellar Bands—a set of absorption features[33] which have puzzled astronomers and spectroscopists for more than six decades. Because the project was not considered a priority by the cluster group at Rice University at that stage, it had to await a convenient slot in their program.

In the interim, a group at Exxon carried out the basic graphite-vaporization experiment. In the summer of that year (1984) they published a fascinating result: the discovery of a totally new family of carbon clusters C_{30}–C_{190}[34]—

much larger species than those prepared by Walton et al.[12-14] or observed by Hintenberger.[13] This exciting discovery was peculiar because only even-numbered clusters were detected. It is important to note that at this juncture no specific cluster was perceived to be special. In August 1985 (almost 18 months after my visit) Curl telephoned to say that carbon experiments were at long last imminent. He asked whether I wanted to come to Houston to participate or if they should carry out the experiments and send the data to me. One thing was certain in my mind: I had not waited this long to have my experiments carried out by others in my absence; I wanted to do them myself and to direct the operation personally. Therefore I packed my bags and at my wife Marg's expense arrived at Rice University within days.

Second Visit to Rice University—The Discovery of C_{60}

Silicon and germanium cluster studies were on the Rice plate in August 1985 because of their implications for semiconductors. Such experiments were considered to be important because the results might have useful applications (!) The carbon project, on the other hand, was thought to have no possible application (other than for astronomy) and was to be completed quickly, causing as little delay to the semiconductor study as possible. Preliminary measurents on carbon had already been carried out, and the Exxon spectra had been reproduced; nothing untoward was noticed. As soon as I arrived (August 28th) I presented a lengthy informal seminar on everything I knew about carbon in space, stars, and soot. My experiments started on Sunday, September 1st, 1985. I worked in the laboratory alongside two research students, Jim Heath and Sean O'Brien—an exhilarating experience; Yuan Liu was also involved. We toiled late into the night, varying the clustering conditions and monitoring the reactions of the carbon clusters with hydrogen, oxygen, and ammonia—gases which I thought would give rise to polyynylcyanides and other chain molecules. They did! The experiments thus immediately confirmed that the chemistry in red giant stars could be responsible for interstellar carbon chains. Curl and Smalley paid frequent visits to the laboratory. As the experiments progressed it gradually became clear that something quite remarkable was taking place: As we varied the conditions from one run to the next, we noticed that a peak at 720 amu[*] (corresponding to a C_{60} species) behaved in a most peculiar fashion. Sometimes it was completely off-scale; at other times it was quite unassuming. The spectrum recorded on Wednesday, September 4th, 1985 was astounding (Fig. 6). Our reactions were noted in the laboratory record book (Fig. 7a), and I annotated my copy of the printout (Fig. 6). From that point onwards the idiosyncratic behavior of this peak was followed very, very closely (Fig. 7b). When this result appeared, the carbon project—

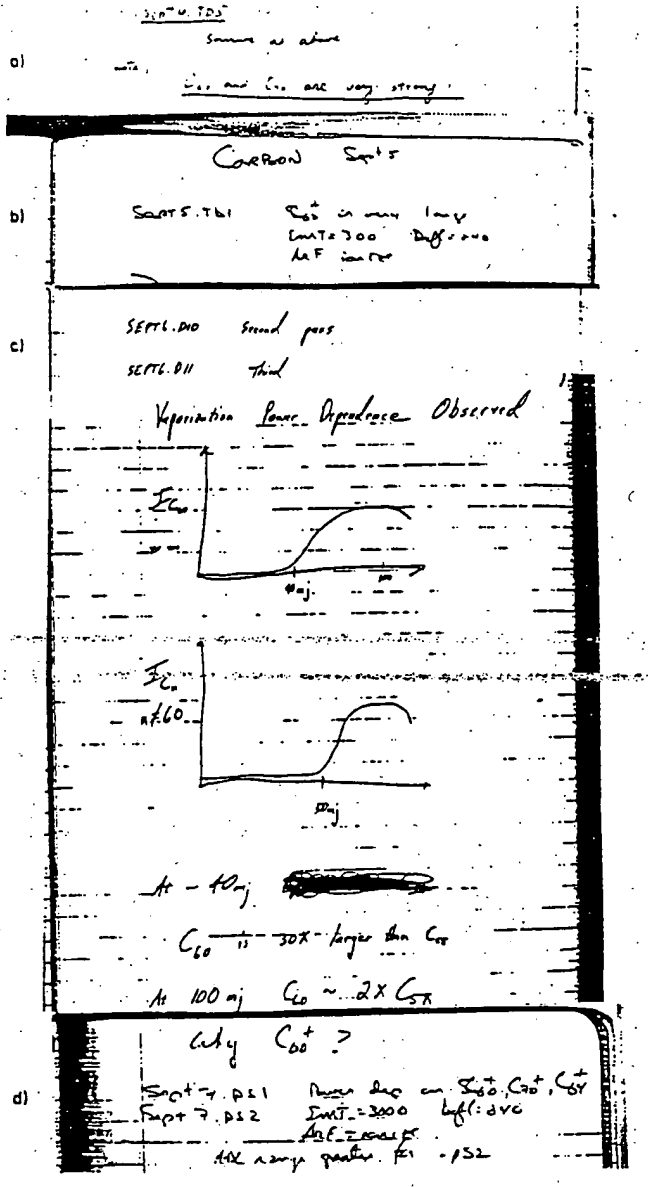

Fig. 7. Entries by Heath, Liu, and O'Brien in the Cluster Laboratory Notebook from the period September 4–7, 1985 when key experiments were carried out at Rice University. a) September 4th: First recorded note that C_{60} and C_{70} were very strong (see also Fig. 6). b) September 5th: C_{60} signal again very strong. c) September 6th: Record of first experiments which specifically aimed at optimization of the conditions for production of a dominant C_{60} signal ("C_{60} is 30 × larger than C_{70}.") d) September 7th: Further power-dependence studies.

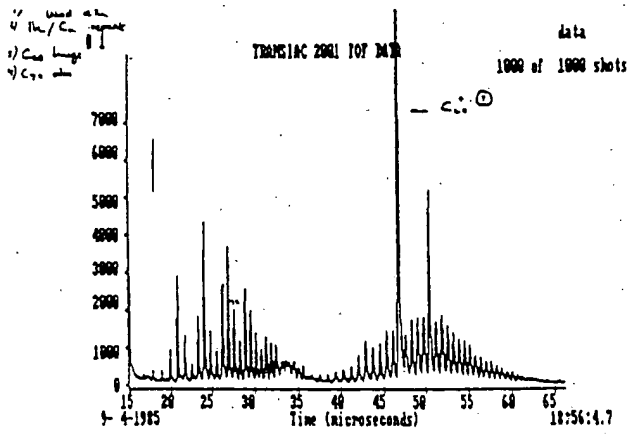

Fig. 6. Annotated time-of-flight (TOF) mass spectrum of carbon clusters produced on Wednesday, September 4th, 1985, the day on which the dominance of the C_{60} signal was first recorded (see also Fig. 7a).

[*] Editorial note: amu = atomic mass unit. According to *Quantities, Units and Symbols in Physical Chemistry* (Ed.: Int. Union of Pure and Applied Chemistry), Blackwell, Oxford, 1989 (Chapter 2.10), amu is the symbol for the unified atomic mass unit m_u and the unit u. In this review the unit amu which is still encountered frequently is used.

for the first time—engendered general interest, and by mutual agreement continuation of the semiconductor program was delayed so that we could concentrate on the remarkable phenomenon which we had uncovered. As the weekend approached our actions, thoughts, and conversations turned more and more to the phenomenon. What might this special "wadge" of carbon be? Smalley had never come across this British term for a cluster and liked it so much that he started to refer to C_{60} as the "Mother Wadge"; the omnipresence of the cluster led me to call it the "Godwadge". On Friday, September 6 during a group meeting, Curl suggested that we should concentrate on identifying the conditions under which the 720 amu peak was most prominent. O'Brien and Heath agreed to work shifts during the weekend. Experiments aimed specifically at optimizing the signal were carried out that same evening, and conditions were immediately found under which C_{60} peak was 30 times stronger than the adjacent C_{58} signal (Fig. 7c). After further optimization (Fig. 7d) the striking spectrum (Fig. 8) was finally obtained. C_{70} is also prominent!

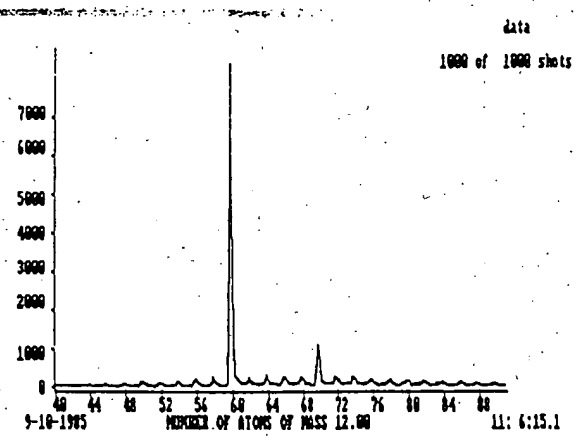

Fig. 8. TOF mass spectrum of carbon clusters under the optimum conditions for the observation of a dominant C_{60} signal.

The Structure of C_{60}(?)

What on earth could C_{60}(?) be? In the days following our discovery of C_{60} (Fig. 6), the signal began gradually to dominate our results as well as our thoughts and conversation. The quest for a structure which could account for this precocious wadge of carbon led to numerous, synergistic [Editorial comment: R. Buckminster Fuller's architectural constructions were based on a vectoral geometry which he called energetic—synergetic geometry. This was founded on a natural philosophy, according to which nature constructs systems of forces such that the maximal strength can be obtained from the minimum effort in construction.] discussions among all five members of the team during those days. The deliberations were particularly intense on Monday, September 9th. As this day wore on and all the ideas which had surfaced during the period were assessed and reassessed, a consensus grew that C_{60} might be some sort of spheroid. One possibility we considered was that the laser had blasted flakes of hexagonal carbon from the graphite surface, and that these hot graphite-like networks had somehow wrapped themselves up into closed cages, thus eliminating the dangling edge bonds and making the cage unreactive. This idea had instant appeal for all. For me this concept brought back vivid memories of Buckminster Fuller's geodesic dome at EXPO '67 in Montreal (Figs. 9 and 10). I had actually

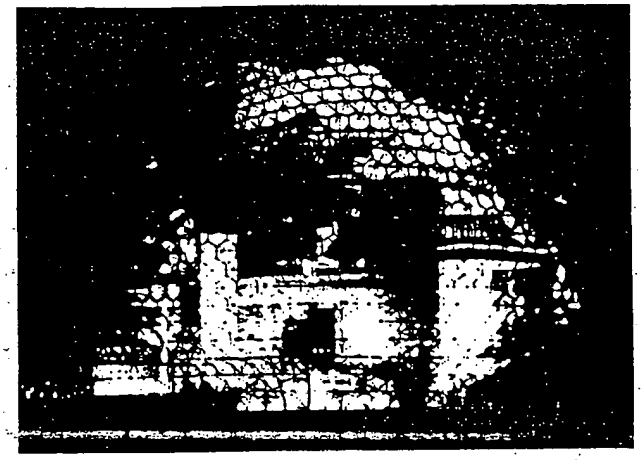

Fig. 9. Photograph (by Michel Proulx) of the geodesic dome designed by Buckminster Fuller for the U.S. exhibit at EXPO '67 in Montreal (taken from *Graphis* 1967, *132* 379). One of the pentagons necessary for closure is discernable in this photograph.

been inside this remarkable structure at that time and remembered pushing my small son in his pram along the ramps and up the escalators, high up among the exhibition stands and close to the delicate network of struts from which the edifice was primarily constructed. This experience had left an image in my mind which could never be erased. I had collected numerous photographs of the dome from magazines over

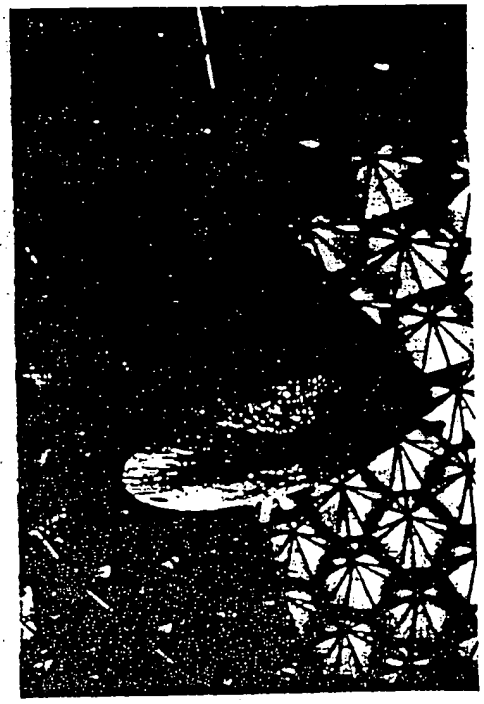

Fig. 10. Photograph (by Robin Whyman) of the inside of the EXPO '67 dome in Montreal. One of the pentagons necessary for closure is clearly visible in the middle section, as is the way in which the strut lengths have been adjusted to achieve a smooth round shape.

Fig. 11. The two cardboard polyhedra which played key roles in our search for the structure of C_{60} (see text). Left) stardome map of the sky (Buckminster Fuller patented i-icosahedral and other polyhedral world-map projections); right) Smalley's model with 60 vertices and 12 pentagonal and 20 hexagonal faces.

the years from Life, Paris Match, and Graphis. Particularly striking were those in my favorite graphic art and design magazine, Graphis, to which I had subscribed since my university days. As I remembered it, the Graphis pictures (Fig. 9) showed that the dome consisted of a plethora of hexagonally interconnected struts. Indeed, the dome had actually initiated my interest in some of Buckminster Fuller's other projects; I had even been in the process of writing to him with a view to working with him on the organized growth of massive urban structures. However, I did not pursue this, because I was offered a permanent academic position at Sussex at just that time.

As far as C_{60} was concerned, I wondered whether Buckminster Fuller's domes might provide some clue. Smalley also strongly favored some sort of spheroidal structure and suggested that we borrow a book from the Rice University library. We obtained a book by Marks[35] in which geodesic domes of all kinds were described. In addition I had one or two other structural proposals which intrigued me: One was a four-deck model 6:24:24:6 (two coronene-like sheets sandwiched between two benzenoid ones) with a roughly spheroidal shape. It contained 60 atoms, and its symmetry suggested that the dangling bonds might be somewhat deactivated. However, I really could see no reason why this species would be as unreactive as C_{60} appeared to be; a closed-cage solution would certainly be more stable. A second image came to mind several times, most vividly on this particular Monday. This was of a polyhedral cardboard stardome (Fig. 11 left) which I had constructed many years before when my children were young. This map of the stars in the sky was tucked away in a cardboard box (that universal quantum of storage) downstairs in my home far away in England. I itched to get my hands on it and even described its features to Curl at lunch time. I remembered cutting out not only hexagons but also pentagons. I wondered whether I should telephone my wife to ask her to count the vertices in order to ascertain whether, as I half-suspected, they totaled sixty.

The Mexican Restaurant

I was due to return to the UK the next day, so that evening (Monday, September 9th) I thought we should celebrate our extraordinary discovery. I invited the group out to dinner at what had become our favorite Mexican restaurant. During the meal the conversation was naturally dominated by C_{60}(?). We again considered all the ideas which had come up in our deliberations during the days that had passed since the signal had first been noticed. We agreed unanimously on a *closed cage* structure. We talked about Buckminster Fuller's domes, Smalley, about chicken-wire cages, and I reiterated the essentials of the stardome—its spheroidal shape, hexagonal faces, and, in particular, the pentagonal faces. Smalley expressed an interest. After the meal other members of the group went home; I returned to the laboratory in order to study the Marks' book on Buckminster Fuller, but I could not find it. I again considered telephoning home about the number of vertices in the stardome. But it was now far too late since it was well after midnight in the UK.

Very early the next morning Curl telephoned to say that Smalley had experimented with paper models based on the stardome characteristics I had mentioned the previous day. Smalley had come up with something bigger than anything he (Curl) had ever been involved with before. When I got to the laboratory and saw the paper model (Fig. 11 right) which Smalley had constructed during the night I was ecstatic and overtaken by its beauty. It seemed identical to the stardome as I remembered it, and I was quietly pleased that my conjecture had been right all along. Heath and his wife Carmen had also experimented with a geodesic structure modeled out of jelly beans and toothpicks; it was not quite so convincing.[36]

In summary, the quest for a rational explanation of the dominant line in the mass spectrum had reached a climax on Monday, September 9th. Ideas were suggested, refined, or critized in earnest throughout that final day. Buckminster Fuller's domes were invoked, Marks' book was consulted, and the stardome's pentagonal faces introduced at midday

and again in the evening; Smalley and the Heaths experimented further with models during the night after our meal. All this took place in a matter of hours, leaving no time for anything important—other than perhaps Marks' book—to "slip through the cracks".[37] It was most satisfying that synergistic (a Fullerism) teamwork had been involved in the experimental observation as well as in the positing of the structure.

I delayed my flight home for one extra day (until Wednesday, September 11th) in order to help to write the publication. At one point Heath was sitting at Smalley's desk when the telephone rang. A mathematician, whom Smalley had consulted earlier to ask about the structure, informed Heath, "Tell Rick—it's a soccerball!" Almost unbelievably, until that moment, none of us had realized that the C_{60} structure we were proposing had the same symmetry as the modern soccer-(USA) or football (rest of the world). I do not know how I could have been so blind—my only (feeble) excuse was that the modern football was introduced after I ended my serious soccer-playing days. The other members of the team could be excused, since a structure related to the American football really was an unlikely contender, at least at that stage. We immediately purchased a real football and our five-a-side team posed for a photograph (Fig. 12). I also

Fig. 12. The five-a-side Rice/Sussex football team (from left): O'Brien, Smalley, Curl, Kroto, and Heath.

photographed Smalley's paper ball (Fig. 11 right), but when I queried the whereabouts of the Heath model in order to photograph it for posterity, I was informed that it no longer existed because Mary-Joe (another Rice graduate student) had eaten it. So all tangible record of a truly remarkable edifice was lost for all time.

Since the geodesic dome concepts had played such an important part in helping us to arrive at the solution (at least as far as I was concerned), I suggested that we name the compound buckminsterfullerene. Smalley and Curl fortunately agreed, accepting that though the name was long, it did indeed roll smoothly off the tongue. Thus we avoided the fearful international conflict over terminology which would have raged had we named it after a certain well-known ball game. Smalley could not resist putting some alternative suggestions for names at the end of the publication. The name engendered the occasional mild criticism[38] which was dispatched with a little help from Shakespeare.[39] Now that some time has passed, it is satisfying to note how instructive (about geodesy) others have found the name and how flexible it has turned out to be. The whole family of closed cages can be appropriately named—fullerenes.[40] The paper[41] was dispatched by Federal Express to the journal *Nature* on the afternoon of Wednesday, September 11th, 1985.

Five Long Years in the Desert

The ten-hour nonstop flight home to England was a physical and psychological high for me. My first action upon entering the house was to open the cardboard box and take out the stardome which had influenced my deliberations during the search for the structure of C_{60}. It had always looked beautiful; now it positively glowed. When the news of our result spread, Martyn Poliakoff at Nottingham wrote that his friend, David Jones, had already thought of hollow carbon cages. In 1966 Jones had written a delightful article under the pseudonym Daedalus in the journal *New Scientist*[42,43] in which he had suggested that the high-temperature process in the production of graphite might be modified to generate graphite balloons. This was a typical example of the presciently "crazy" ideas of Jones. I thus learned about the Euler principle, which says that 12 pentagons are needed to close a network and that hexagons alone just will not do. I was introduced to D'Arcy Thompson's elegant book[44] and learned that one could close an even-numbered carbon cage with any number of hexagons (except one, I subsequently learned) provided 12 pentagons were included in the network. The beautiful Aulonia (Fig. 13 photograph from Tibor Tarnai) already knew more than we about these simple (pentagonal) facets of (its) life. This was all fun and truly

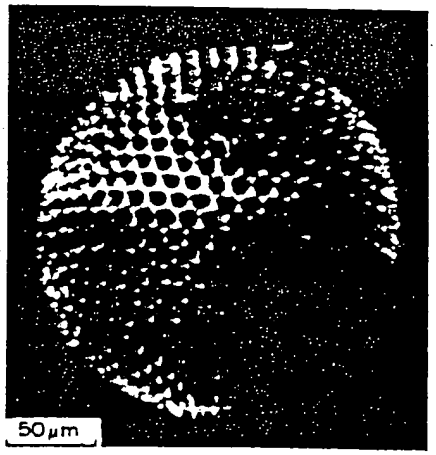

Fig. 13. A siliceous sea creature, *Aulonia hexagona*, appears at first glance to possess a skeleton composed completely of hexagons. Pentagonal structural elements are discernable, however (photograph supplied by Tibor Tarnai).

fascinating, because it became clear that there might even be other (even-numbered) carbon cages—there were certainly other (even-numbered) peaks (Fig. 6), in particular C_{70}. O'Brien and Smalley reached the same conclusions independently. Particularly important were a series of reactivity ex-

periments carried out by O'Brien, ... showed that all the even-numbered carbon species were totally unreactive, a result neatly commensurate with closed structures for all the even-numbered cages.[45]

I met David Jones, a most fascinating individual, who epitomizes so much of what the spirit of science should be about. We also learned that Osawa and Yoshida had already thought of C_{60} in 1970 and had even suggested that it might be superaromatic.[46,47] In 1973 Bochvar and Gal'pern[48] also published a theoretical paper on the molecule. Thus it transpired that although there were some most imaginative scientists around, few—other than Orville Chapman at the University of California at Los Angeles (UCLA)[49]—had noticed these pioneering flights of imagination.

Circumstantial Evidence for the Identity of the "Third Man"

The first question stimulated by the realization that we might have found a "third form of carbon" with a hollow, cage structure was obvious: is it possible to trap an atom inside the cage? My early Sheffield background led me to wonder whether iron might form an intriguing ferrocene-like analogue. The day I left, Heath tried to encapsulate iron without success, but the next day he succeeded in detecting a stable $C_{60}La$ complex.[50] This experiment provided the first convincing piece of evidence to support our proposal of the cage structure. Then began what was to become a truly exhausting schedule for me: Every four to six weeks I flew to Houston, and after two to three weeks' work with the group at Rice I returned to the UK and my commitments in Sussex. As soon as I arrived in Houston I would present a group seminar based on ideas which I had developed while in the UK. This schedule continued until April 1987. From the outset the joint Rice/Sussex follow-up program had two clear objectives. First, to make enough C_{60} to prove beyond doubt that our structure was correct and second, to measure the optical spectrum of C_{60} which we had surmised might in some way be responsible for the Diffuse Interstellar Bands.[41] These astronomical features had of course been partly responsible for the carbon-cluster experiment in the first place. These goals were all-consuming and we often talked about "the little yellow (Smalley's guess) or pink (my guess) vial" of C_{60}.

During the late 70s and early 80s I felt that it was simply not enough just to detect the carbon chains; the source must be tracked down. This obsession with the source led ultimately to the discovery of C_{60}. After 1985 I developed a similar attitude to C_{60}. Our discovery of a species which probably had a truncated icosahedral structure was "not enough", and as months and then years passed, confirmation of the structure and its identification in space also became somewhat of an obsession. We (the Rice group and myself) were convinced from the outset that our proposed structure was correct; surely it was too beautiful and perfect to be wrong. However, if for once aesthetics were misleading us, it would be much better if we proved our model wrong ourselves. It is certainly fair to say that the proposed structure was greeted with scepticism by some, though many loved C_{60} and were convinced that we were right from the start. During this pe... (1985–1990) I examined the problem independently at Sussex, as well as in collaboration with the Rice group, who also made independent studies. In time all these efforts resulted in a mass of convincing evidence in support of our proposal.

From the moment we discovered that C_{60} was stable I had one all-consuming dream: I wanted so solve the molecule's structure by NMR spectroscopy. Because all 60 carbon atoms in buckminsterfullerene are equivalent, the ^{13}C NMR spectrum should consist of a single line. Proof of our radical proposal in such an exquisitely simple manner was to remain elusive for some five years; this goal was almost like a holy grail—far, far beyond reach. I was quite convinced that a clever young organic chemist would accomplish this task. I had one consoling thought, namely that we had been rather successful in the past with a series of molecules whose identifications were based on spectra consisting of single lines: Phosphaethene, $CH_2=PH$ (the first phosphaalkene made) had been assigned by its $J = 1 - 0$ microwave line[1,4] and HC_5N and also HC_7N had both been originally single radioline detections in space.[20,22] Then there was, of course, the 720 amu peak in the mass spectrum of C_{60}.[41] How fitting it would be to round it all off by *proving* by another *single* line that C_{60} was buckminsterfullerene.

C_{70} and the Fullerene Family

It is fair to say that I (and perhaps also my colleagues at Rice University) occasionally woke up in the middle of the night and wondered whether I should have to commit suicide if our idea turned out to be wrong. Had we stuck our necks out too far? These thoughts only lasted seconds. I would reassess all the evidence, realize that everything fitted, and go back to sleep convinced more than ever that C_{60} had to be a geodesic cage. Time pased, we made several advances,[51,52] and each time the cage concept clarified our observations. That was important. I remembered hearing Richard Feynman on BBC radio say that it seemed to him that if a radical new theory were right, it would allow the solution of previously unsolved puzzles. I quantified this: If an idea fitted 80–90% of the observations, it was almost certainly right; if more than 10–20% of the details had to be bent to fit, it was almost certainly wrong. Buckminsterfullerene was well up in the first category.

I remember vividly the day on which all my lingering doubts vanished. I was sitting at my desk thinking about the reasons why C_{60} might be stable. The missing piece of evidence in this personal jigsaw puzzle turned out to be so simple, it was almost child's play; indeed it evolved from my playing with molecular models of various conceivable cages. The solution was related to the C_{70} signal which always popped up prominently when C_{60} was strong. I used to call the two species "the Lone Ranger and Tonto"[*] because

[*] The Lone Ranger und Tonto were a famous cowboy and Indian duo from the movies. As a child I saw them every week fighting crime in the Wild West. Bob Dylan immortalized them in the following blues text:
Well the Lone Ranger and Tonto
They are ridin' down the line
Fixin' ev'rybody's troubles
Ev'rybody's 'cept mine.
Somebody must a tol' 'em that I was doin' fine.

they were so inseparable and because C_{60} was always dominant (Figs. 6 and 8). As far as C_{60} was concerned, it seemed no accident that the modern soccerball with the same layout is one of the most, if not *the* most, resilient of constructs, able to survive being kicked around the world (and perhaps around the galaxy). Maybe the football held a simple clue. When I looked carefully at a football, I was struck by the fact that all the (black) pentagons are isolated, whereas all the (white) hexagons are linked. It is known that unsaturated compounds composed of abutting pentagons (the pentalene configuration, Type II, Fig. 14), without substituents which allow extended conjugation, tend to be unstable. Curiously, a compound with just such a structure appeared on the cover of *Angewandte Chemie* (July 1987) that very week.

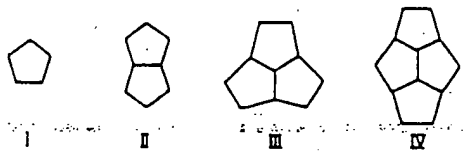

Fig. 14. Isolated and abutting pentagons: I, isolated; II, fused pair (pentalene configuration); III, symmetrically fused triplet (triquinacene configuration); IV, directly fused quartet [53].

Since Euler's law requires 12 pentagons for closure, it was also clear that C_{60} was the smallest carbon cage for which all the pentagons could be isolated. O'Brien's reactivity experiments had convinced us that closure was possible, even probable, for all the even clusters. I conjectured that a *pentagon isolation rule* could be formulated to account for the stability[53]; then I began to wonder which was the next cage for which pentagon isolation was feasible.

By playing with the models I saw immediately that it was not C_{62}, and as I added more atoms, try as I would, I could not find cage structures for C_{64}, C_{66}, or C_{68} without abutting pentagons. We had already proposed a structure for C_{70},[50] after Smalley had shown that by splitting C_{60} into two C_{30} hemispheres a ring of ten extra carbons could be neatly inserted, producing a most elegant, symmetric, egg-shaped structure (Fig. 15 right). Suddenly I realized that perhaps this C_{70} cage was the next structure after C_{60} which could close and which also had *isolated* pentagons (Fig. 15). This surprised me. Perhaps closure *necessitated* that 70 be the second magic number! We had stuck our necks out with the C_{60} hypothesis on the basis of a single peak in the mass spectrum, but it now seemed that the cage concept positively insisted that C_{70} *as well as* C_{60} are special.[53] That would be wonderful. A second solution which required both of these particular magic numbers was impossible to conceive, especially since 70 would be an unusual number to be deduced as magic at all, let alone the second in order. I knew that nature would not be that perverse, and thus for first time my conviction that our structure was correct became absolute, and I never again doubted that one day we would be vindicated. Indeed in my opinion this result meant that we were home and dry.

I was elated by this line of reasoning, but I really needed proof. I remembered that Tom Schmalz and his colleagues, Klein and Hite, in nearby Galveston had published some elegant graph-theoretical studies on the fullerenes. I contacted him and asked him what he thought about my idea. I was amazed and delighted when he told me that they had been looking at this same problem and had proven that cages composed of 62, 64, 66, and 68 atoms cannot be constructed without abutting pentgagons.[54] So it was true! I told him that I wondered whether the semimagic C_{50} might be the smallest cage able to avoid abutting triplets of pentagons (Type III, Fig. 14, Lit.[53]). Schmalz et al. subsequently showed this also to be correct.[54] One Sunday afternoon, sitting in front of the molecular models strewn all over our coffee table at home, I decided to investigate other semimagic numbers. I wondered about C_{32} which had been shown by the group at Rice University to be the first cage relatively stable towards photolysis. I toyed with the idea that it might be the smallest cage able to avoid fused quartets of pentagons (Type IV, Fig. 14). I tried to make the smallest model containing such a structure, and as I counted up the atoms I suddenly realized, that it was not C_{32} but a delightfully symmetric C_{28} cage (Fig. 16). I became excited because I

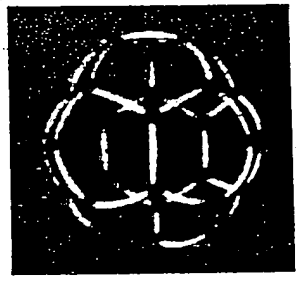

Fig. 16. Molecular model of C_{28}, one of several fullerenes (with 24, 28, 32, 50, and 70 atoms) predicted to be stable on the basis of geodesic and chemical considerations [53]. These magic-number predictions fitted almost perfectly the observations made under certain clustering conditions [51, 55] (see Fig. 17).

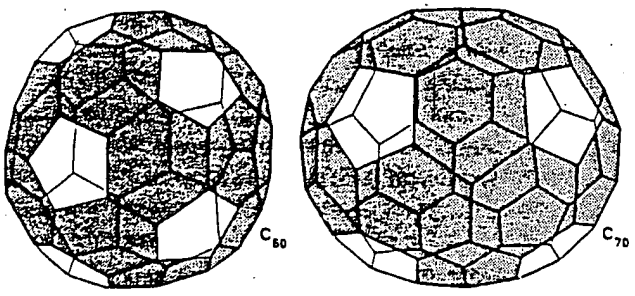

Fig. 15. For species with less than 72 atoms these two structures are the only ones which can be constructed without abutting pentagons. Thus on the basis of the *pentagon isolation principle* and geodesic considerations C_{60} and C_{70} are predicted to be the first and second magic fullerenes. This result together with Figure 8 provided the simplest and strongest circumstantial evidence supporting the closed-cage concept.

knew, that during the Rice/Sussex collaboration period we had occasionally obtained mass spectra in which C_{28} was almost as dominant as C_{60}. At this point it seemed that essentially all the magic numbers would fall into place if these clusters were *all* cages. In particular, I found that I could explain the fascinating spectrum (Fig. 17) published by the Exxon group.[55] Here was all the proof I needed to convince myself that a whole family of cage molecules was sitting around waiting to be discovered. The first somewhat

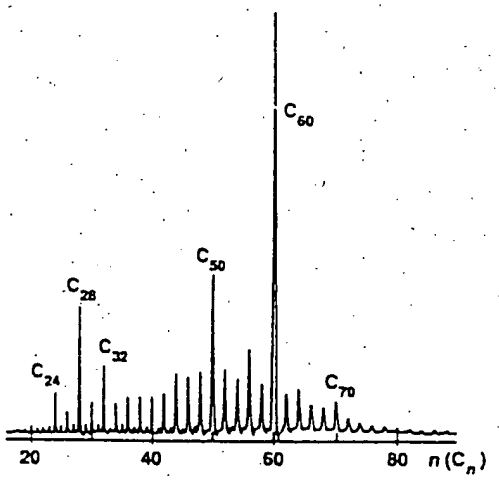

Fig. 17. The particularly interesting mass spectrum of C_n clusters obtained by Cox et al. [55]. The correspondence with the magic fullerene sequence 24, 28, 32, 50, 60, and 70 [53] was the most convincing evidence for the existence of the fullerene *family* prior to the extraction breakthrough. The sharp cut-off at 24 is particularly convincing, since no C_{22} fullerene can exist.

stable member of the family appeared to be C_{24}. This can be explained by the fact that C_{22} cannot exist (I am indebted to Patrick Fowler for pointing out this fact to me) and that C_{20} is the smallest cage and as it has no hexagons at all, almost certainly the least stable. To some extent C_{28} (Fig. 16) became my own personal favorite, because regardless of which of the four threefold axes one views this tetrahedral molecule along, it looks uncannily like Gomberg's famous free radical, triphenylmethyl; this also just had to be right. I knew about Moses Gomberg's discovery from my favorite organic text (Fieser and Fieser[56] which Harry Heaney, my chemistry teacher in school, had encouraged me to buy and read so long ago). It had always amused me to think that on attempting to make the rather mundane compound hexaphenylethane, Gomberg failed (miserably), produced the triphenylmethyl radical, and had to be consoled with becoming known as the father of free radical chemistry instead. This was the sort of "failure" that really appealed to me. If C_{28} is relatively stable, then $C_{28}H_4$ should be a fairly stable hydrofullerene. This seemed not at all farfetched; after all, dodecahedrane which Paquette and co-workers first made[57] is basically the perhydrofullerene of dodecahedrene (fullerene-20), the simplest and probably the least stable of all the fullerenes since it contains no hexagons. At this time I had a telephone conversation about nomenclature with Alex Nickon in which we came to the conclusion that the name "fullerenes" would work well for the family of carbon cages.[40, 53] I gained much satisfaction from the refined concept which was even more appropriate, because Buckminster Fuller had patented constructs of all shapes and sized based on the 5/6 ring principle;[58] some were very similar to the elongated framework of C_{70}. Nickon was just finishing his entertaining book with Silversmith on the origins of the trivial names of compounds.[40]

In Houston a particularly important series of experiments was carried out by Curl, Smalley, and their co-workers which offered further overwhelming evidence for closed cages.[52] One of these was a photofragmentation experiment which provided even-numbered products. Curl had worked out a neat way of explaining how the cages might "spit out" even-numbered (2, 4, 6, ...) carbon chains and then reseal.

Another most convincing study showed that when the encapsulation of atoms of various sizes appeared to be successful, the smallest caged species detectable had diameters commensurate with the known sizes of the encapsulated atoms.

C_{60} and Soot

During one of my eight visits to Rice University between August 1985 and April 1987 we considered carefully the reactivity results and developed a hypothetical mechanism for the formation of C_{60}.[45] Heath, O'Brien, and I spent hours in the library digging through an excellent selection of books and journals on carbon. The final version of the mechanism grew out of intense synergistic group discussion. It was also clear that the mechanism might explain soot formation as well. After all in a review on soot, Harris and Weiner[59] had pointed out the complete absence of knowledge of the chemistry involved in soot formation. Thus a fresh idea probably would be welcome. Our mechanism implied C_{60} should be a by-product of soot formation. Curl was apprehensive about introducing the word soot, especially in the title. How prescient were his worries! However, Smalley and I decided to throw caution to the wind—after all, when you have gone as far as you can go (in postulating C_{60} formation in a chaotic plasma), you might as well go further. Our paper met with some criticism.[60] To our delight, however, in 1987 we heard that Klaus Homann's group in Darmstadt discovered that C_{60} was a dominant ion in a sooting flame.[61] (Note: Very recently, a careful study by Howard's group at the Massachusetts Institute of Technology has shown that up to 7% of the soot from a benzene flame consists of fullerenes.[62])

The Giant Fullerenes

One day I decided to spend £300 on ten-thousand sp^2 carbon atoms (molecular models!) The odd eyebrow was raised at Sussex when I said that I was buying them just because I wanted to see what giant fullerenes such as C_{6000} (with a diameter ten times that of C_{60}) looked like. Ken McKay (a graduate student) obtained Coxeter's book[63] and Goldberg's paper[64] and set to work. When he came into my room with models of C_{240} and C_{540} (Fig. 18), I was delighted but perplexed—they were beautiful, but not at all what I had expected. C_{540}, in particular, was not round like Buckminster Fuller's domes, but in fact much more interesting: It was essentially a monosurface which swept between cusps in the vicinity of the pentagons; it had icosahedral symmetry, but was not an icosahedron.[65] Then we realized that its shape might explain[65] the polyhedral patterns in graphite microparticle electron microscope pictures published by Iijima (Fig. 19).[66] The structure of these microparticles could be nicely explained as concentric shells of graphitic carbon in which the shells had giant fullerene shapes. Few of our discoveries have delighted me more than these objects, partly because they are so elegant, but also because the exercise, which was started *purely* for fun and with no serious aim, had yielded such an apparently important result. It was also an object lesson, since I had assumed

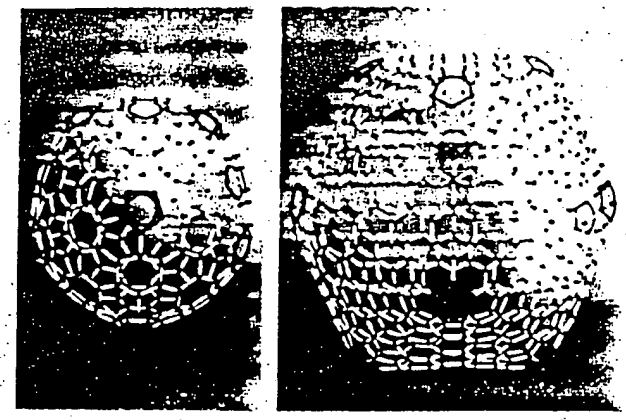

Fig. 18. Molecular models of the giant fullerenes C_{240} (left) and C_{360} (right). The models possess icosahedral shapes rather than perfectly spheroidal ones similar to the geodesic domes. Each of these structures can be considered as an initially flat hexagonal network which has warped into a closed monosurface (of icosahedral symmetry) by 12 pentagonal disclinations giving rise to the cusps.

that the giant fullerenes would be spherical like Buckminster Fuller's domes and had not looked carefully at Iijima's images. Even the most spheroidal giant fullerene (Fig. 19 a) was clearly polyhedral (Fig. 19 b). To see what one wants to see

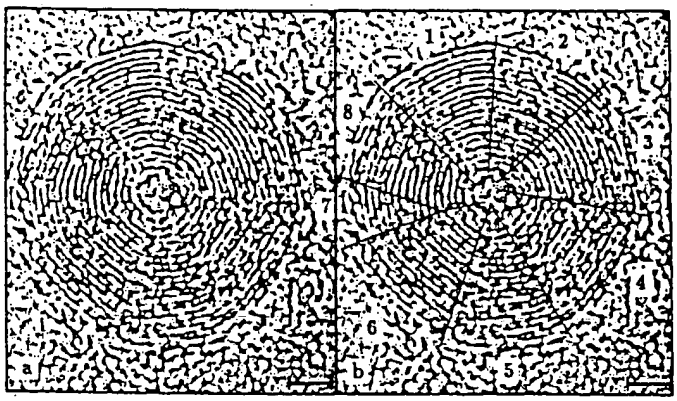

Fig. 19. The image obtained by electron microscopy of an onionlike graphite microparticle observed by Iijima [66] which appears superficially to be spheroidal (a). Careful scrutiny of this image, however, indicates that the object has a polygonal outline consistent with a set of concentric quasi-icosahedral fullerene-like shells (b) [65]. The marker indicates a scale of 20 Å.

rather than what is, is a cardinal sin for a scientist and the temptation is to be resisted at all costs.

The Quest for C_{60}

Until late 1989 the evidence in support of our structure proposal was, to my mind, very convincing, but it could not be deemed anything other than circumstantial. Clearly a macroscopic sample of C_{60} was needed—not just a whisper in a supersonic helium wind, detectable only by that ultrasensitive sensor, the mass spectrometer. At Sussex we sought more tangible evidence. The Science and Engineering Research Council (SERC) funded the construction of a cluster-beam apparatus, which was assembled with Tony Stace; Steve Wood helped us to obtain financial support from British Gas in the form of Collaborative Award in Science and Engineering (CASE) studentship for combustion-related studies. It was this assistance which was ultimately our salvation (vide infra). In a third project conducted with Ken McKay, we probed (by electron microscopy) the films produced by a carbon arc under helium in an old bell jar evaporator. We found that the film microstructure changed as the helium pressure was increased (to ca. 50 mmHg). The quadrupole mass spectrometer, with which I sought to monitor whether C_{60} was produced in this experiment, was the integral part of a modest carbon materials research project which failed to attract support from any funding source (including chemical companies). Because Stace and I had been quite generously funded by the SERC solely for the cluster-beam studies, another application (and indeed a rather applied one) to that source was difficult. Time slipped by and this program faltered even though I had put a great deal of effort into trying to obtain financial support.

The First Paper by Krätschmer, Fostiropoulos, and Huffman

In September 1989 Michael Jura (UCLA Astronomy Department) sent me a copy of a thought-provoking paper[67] (Fig. 20) presented by Krätschmer, Fostiropoulos, and Huffman at a symposium on interstellar dust. This research group from Heidelberg and Tucson had observed four weak but distinct infrared absorptions in a film of arc-processed graphite, which were tantalizingly consistent with the expected spectrum of buckminsterfullerene. From theoretical studies[68] it was known that C_{60} should exhibit only four lines. What was more, the observed frequencies agreed quite well with those predicted. I had long followed the work of this group and knew that they had developed great expertise in studying carbon by spectroscopy. We had occasionally tried related studies, and I was only too aware of how tricky they were. I was sceptical about their result and also rather cha-

Harry - Presented at Capri -
Do you believe this? -H.

SEARCH FOR THE UV AND IR SPECTRA OF C_{60} IN LABORATORY-PRODUCED CARBON DUST

W.Krätschmer, K. Fostiropoulos *Max-Planck-Institut für Kernphysik, Heidelberg, W.-Germa*
and
D.R. Huffman *University of Arizona, Tucson, Arizona, USA*

Carbon dust samples were prepared by evaporating graphite in an atmosphere of an inert quenching gas (Ar or He). Changes of the spectral features of the carbon dust were observed when the pressure of the quenching gas was increased. At low pressures (order 10 torr), the spectra show the familiar broad continua. A high pressures (order 100 torr), narrow lines in the IR and two broad features in the UV emerge. The four strongest IR features are located in the vicinity of the lines predicted for the C_{60} molecule. One of the observed UV features may be related to the known 368 nm transition of C_{60}. It thus appears that at high quenching gas pressures C_{60} is produced along with the carbon dust.

Fig. 20. Annotated copy of the key paper presented by Krätschmer, Fostiropoulos, and Huffman at the conference *Dusty Objects in the Universe* in Capri (1989) [67]. This paper with the appended query was sent to me by Michael Jura (UCLA) who attended this conference.

grined. for had not Ken McKay and I made soot in a bell jar in exactly the same way three years before during the project, which we were forced to abandon through lack of funds?

I decided to resurrect the old and decrepit bell jar and with Jonathan Hare (holder of the British Gas CASE graduate studentship) tried to reproduce the infrared features obtained by Krätschmer et al. Michael Jura's missive arrived around September 1989, just before the start of the Sussex academic year, a time when third year undergraduate projects are needed. It does not matter whether these projects yield results: they should imbue the student with the flavor and excitement of genuine research, that is, the experience of working in the dark, not—as all too often happens—the frantic scramble for results at all costs! I had often initiated the most speculative of projects in this way, and my experience had shown time and time again that important and exciting studies could often start from such inauspicious beginnings. It seemed perfect for Amit Sarkar's third-year project, and he joined Hare on this wildly speculative project. Fairly soon these students succeeded in obtaining the IR bands (Fig. 21), which, although always very weak and highly irreproducible, confirmed the observations of the group from Heidelberg and Tucson. The obsolete apparatus they

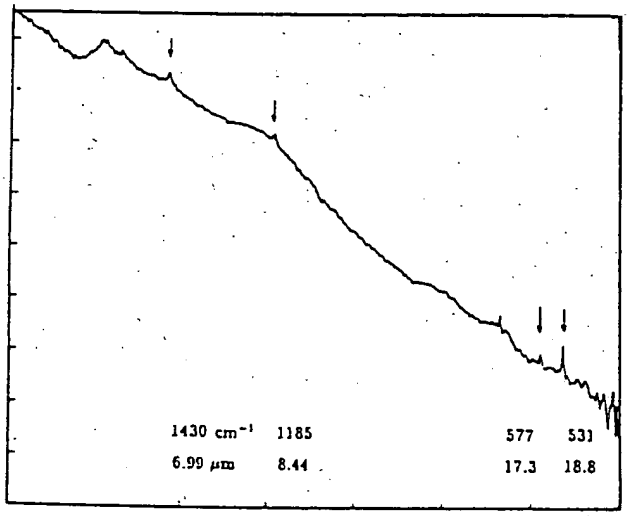

Fig. 21. Infrared spectrum of a film of arc-processed carbon obtained by Hare and Sarkar at Sussex which shows weak but clear (and confirmatory) evidence that the features first observed by Krätschmer et al. [67] (see Fig. 20) and tentatively assigned to C_{60} were real and repeatable.

promptly fell to pieces! After rebuilding it almost completely from scratch, Hare tried to repeat the earlier observations, but consistent results eluded him. Sometimes he obtained the characteristic spectral features, sometimes they disappeared for days or weeks at a time. In retrospect, I suspect that the original discovery of the IR features by Krätschmer et al. could have been made by few other groups. Hare carefully varied every experimental parameter he could think of and finally developed the expertise to produce films which exhibited the telltale infrared features consistently. He wrote to Krätschmer about his efforts and received an encouraging reply containing useful advice. This certainly helped, because it was quite difficult to make films amenable to analysis.

The Dimerization of C_{30}

I spent about one month in the UCLA Astronomy Department around Easter 1990. One day, Mark Morris brought François Diederich from the Chemistry Department to see me. Diederich appeared excited and exhorted me to come to his office because he had something to show me. In response to his manner I somewhat disdainfully quipped, "You've not made C_{60}?" When he replied, "How do you know?", I was startled and suddenly became apprehensive since there was genuine surprise in his voice. When we arrived at his office he showed me an astonishing mass spectrum. In their attempts to make a pure carbon ring of 30 atoms Diederich, Rubin, Whetton, and their co-workers, had found that the molecule spontaneously dimerized to form C_{60} with almost unbelievable efficiency.[69] This staggering result seemed to answer, almost at a stroke, many puzzling questions that had been on my mind for years about carbon chains, their relationship with C_{60}, and soot. But I became even more apprehensive when I comprehended that the UCLA group might be on the verge of obtaining the coveted C_{60} NMR line. Subsequent discussions with David Walton, with whom I had probed aspects of the C_{60} formation mechanism,[70] alleviated my worries; he convinced me that scaling up the UCLA experiment so as to produce sufficient C_{60} for the key NMR measurement presented an anormous challenge.

Mass Spectrometry

I returned to Sussex and by early summer 1990 started to believe for the first time that C_{60} really might be in our sooty deposit. We therefore decided to probe the material by solid-state magic-angle-spinning (MAS) NMR. Indeed Ken Seddon (a Sussex colleague) had encouraged me to do this some years before. Perhaps the single ^{13}C NMR line was close at hand in the black soot, which at least we could now touch. I considered buying the most isotopically pure ^{13}C graphite, but that would have been very expensive, and we had no

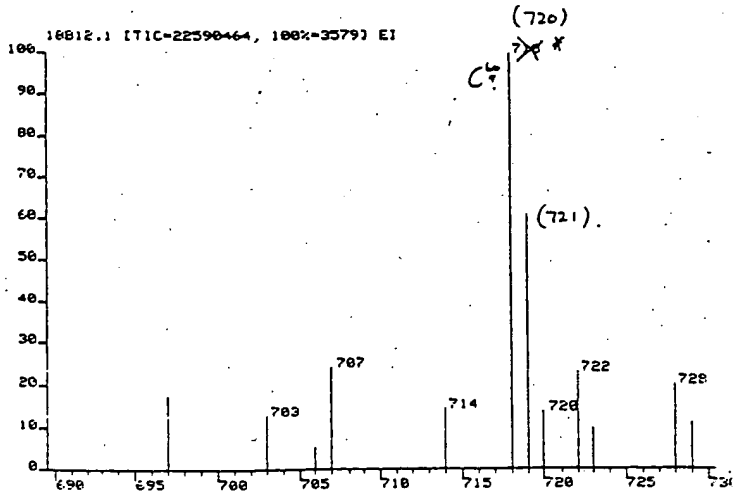

Fig. 22. Part of the FAB mass spectrum of a deposit of arc-processed soot obtained by Abdul-Sada on July 23rd, 1990 at Sussex. The calibration was off by 2 amu; however, the isotope pattern was convincing since the peaks are close to the intensity ratio 1.0:0.66:0.44 expected for $^{12}C_{60}$, $^{12}C_{59}{}^{13}C$, $^{12}C_{58}{}^{13}C_2$.

money anyway. The problem of generating enough material for solid-state NMR from the scrapings of thin sooty films, seemed insurmountable, especially since it was so difficult to produce the films in the first place, let alone analyze them. We really needed another way to monitor the samples, so we tried Fast Atom Bombardment (FAB) mass spectrometry. Ala'a Abdul-Sada helped us, and finally we obtained the mass spectrum shown in Figure 22. The signal containing the ^{13}C satellites was really quite convincing, but I wanted the result confirmed. The entry in Jonathan Hare's laboratory notebook on July 26th, 1990 (Fig. 23 top, second sentence) epitomizes many of our problems and requires little further comment.

The Red Solution

During this period we had considered the properties of C_{60}. What form would the compound take? Would it be a high-melting solid or a liquid? Would it be soluble? Benzene was an obvious solvent, since C_{60} should look like benzene from every side (or at least from 20 sides). I remembered the little pink (or yellow) vial of liquid we used to talk about and wondered if the compound might even be volatile. In addition I had often discussed (with Smalley, Rohlfing, and others) how much C_{60} was being made in our experiments. The rough proportion which always seemed to arise was $< 1:10000$ of the total amount of carbon. At this level, given the amount of soot available, only a supreme optimist would attempt solvent extraction. Fortunately Hare is one—perhaps partly because he is a physicist working among chemists. On Friday, August 3rd Hare made up a mixture of the soot and benzene in a small vial, which he set aside over the weekend (Fig. 23, second entry). When he came in on Monday morning (August 6th) he noted (Fig. 23, third entry) that the solution looked "slightly red(d)ish" (Fig. 24). The generation of a red solution from pure carbon was scarcely believable. Hare made more material during the next few days and attempted mass spectrometric measurements on extracted material for the first time on Thursday, August 9th (Fig. 23, fourth entry).

possible use of FAB Mass Spect. 26/7/90.

Came back from Scotland Walk to find Fab Mass spec had been done with exciting results. unfortunately the machine has been clean so we can't repeat.

Results so far.

Seen decent signal @ (12xC) = 720amu !

also ^{13}C is ~1% of natural carbon so calculations show that for C_{60} we 60% could have One

5.

7/8/90

1) Made up ~ ½ a (30ml) tube of C_{60} + Carbon powder, Actual Volume would be much smaller than this blue powder is so impure.

2) added about 25ml of Benzene and shook mixture

3) allowed to stand for Weekend.

6/8/90

Solution looks slightly reddish, tried to pipet liquid out from top but mixed up.

9/8/90

Vacuum lined sample to about 5th of volume could go lower (ie more concentrated) but we need about this Volume if we want to use IR liquid cell, so will keep to this.

Continued evaporation down to about 4-5 drops (just ?). FAB showed No C_{60} (720).

Fig. 23. Entries by Hare in his laboratory notebook: July 26th, 1990:

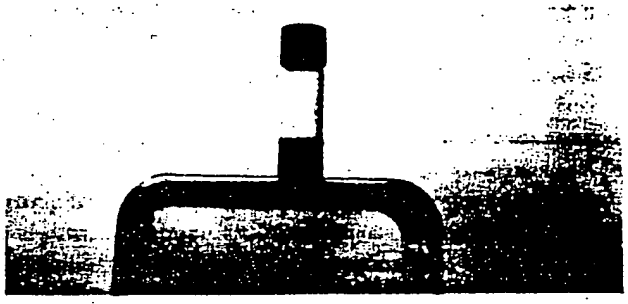

Fig. 24. Original reddish extract obtained on Monday, September 6th, 1990 (see Fig. 23).

About 10 o'clock the next morning (Friday, August 10th) I received a telephone request from the journal *Nature* to referee a paper by the Heidelberg/Tucson group which I accepted. I was totally unprepared for the bombshell which arrived minutes later by telefax. Following up their own earlier work, Krätschmer, Lamb, Fostiropoulos, and Huffman had successfully sublimed from their carbon deposit a volatile brown material, which dissolved in benzene to give a RED SOLUTION (!!!!!).[71] Crystals obtained from this solution yielded X-ray and electron-diffraction data commensurate with material composed of arrays of spheroidal molecules 7 Å in diameter separated by 3 Å, just as expected for buckminsterfullerene. This beautiful paper even contained photographs of crystals. I was convinced that they had isolated C_{60}, and we had been pipped at the post. Somewhat stunned, I pondered our demise and faxed my report back to *Nature* after lunch. I recommended that the paper be published without delay and requested the editor to convey my sincere congratulations to Krätschmer and his associates.

This was what the British call a difficult moment, but as I slowly surveyed the damage I realized that all was not quite lost. It gradually dawned on me that there was not a single(!) NMR line to be seen in the manuscript (nor was there a mass spectrum. We later learned that they had the mass spectrum, but certain problems had arisen which precluded its inclu-

sion in the manuscript.) At this point we had spent nearly a year struggling independently learning how to make the arc-processed material: we had made our own soot, we had confirmed the presence of C_{60} mass spectrometrically, and we had solvent-extracted the red material—and all this *before* the manuscript arrived. I decided that we were not going to abandon our efforts now after we had achieved all this. We still had a lot going for us, and I thought we might be able to obtain the desired NMR result. However, now that the Heidelberg/Tucson study was essentially in the public domain it would be transmitted around the world by telefax within hours. I had studiously tried to avoid such situations in science—competition—all my life; my philosophy is to probe areas in which few others, preferably no one, work. That is where, it seems to me, the most unexpected discoveries are likely to be made.

We had to act very quickly if five years of effort were not to be completely in vain. A race must be on because the material was now so easy to make, and it could not be long before other groups, far better equipped than we, recognized that there was one last exquisite prize remaining in the story of the discovery of C_{60}—the NMR line. Our one priceless advantage was that Hare had already made a reasonable quantity of material, and that, at that moment, only the Heidelberg/Tucson group had any at all. We needed help and fast. Roger Taylor, an organic chemist, provided the desperately needed expertise: he separated the material quickly and efficiently. Since our mass spectrometer had broken down again, Hare rushed by train to Manchester with a sample of the precious extract. Numerous frantic telephone calls passed between Sussex and Manchester, because the sample refused to respond to analysis. Then with a key piece of

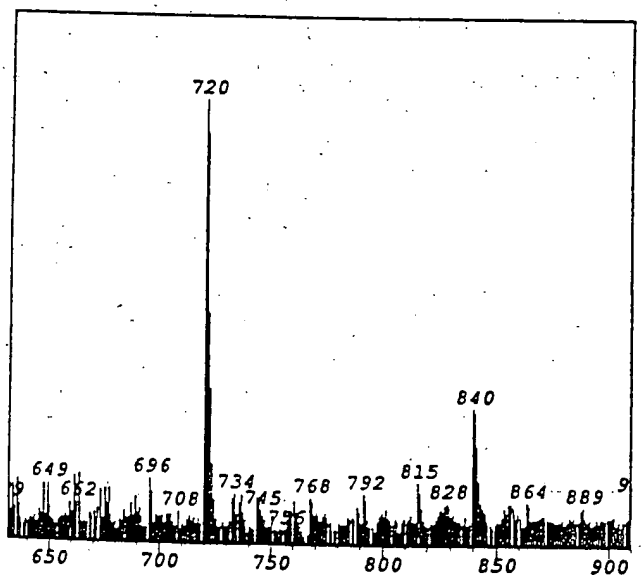

Fig. 25. Part of the FAB mass spectrum of the red extract which confirmed that it consisted mainly of C_{60} and C_{70}. The spectrum also indicates the presence of other fullerenes [72].

advice from Taylor about solubility, the Manchester operators (at Kratos) managed to dissolve the material in the FAB matrix and obtained the FABulous mass spectrum shown in Figure 25. It was hard to believe, but besides C_{60} other fullerenes with 56 to 72 atoms were detected: in particular, C_{70} was abundant. The whole family of fullerenes appeared to be present in the soot, not just C_{60}!

C_{60} is Magenta (Pink?) in Solution

Taylor noted that the extract was soluble in hexane and recognized that he might be able to separate the fullerenes chromatographically. To his delight he found that on an alumina column resolution into two bands, one red, the other magenta, could be achieved. The magenta fraction, (Fig. 26) was a delight to the eye in the delicacy of its color.

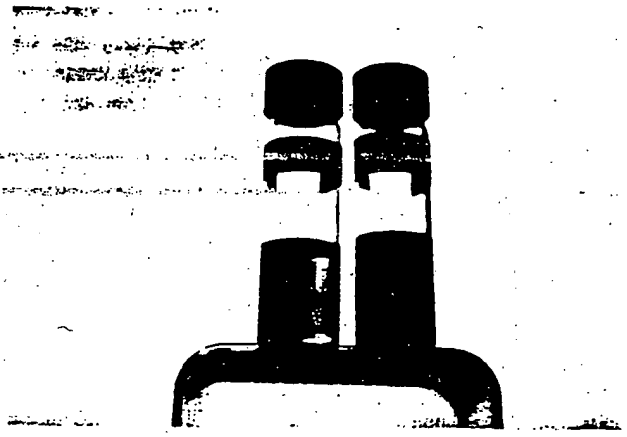

Fig. 26. Chromatographic separation of the red extract by Taylor resulted in a magenta C_{60} fraction (left) and a red C_{70} fraction (right).

Its mass spectrum showed a peak at 720 amu, and we sent the sample to Tony Avent for NMR analysis. We were summoned to see our single line (Fig. 27), which Avent assured

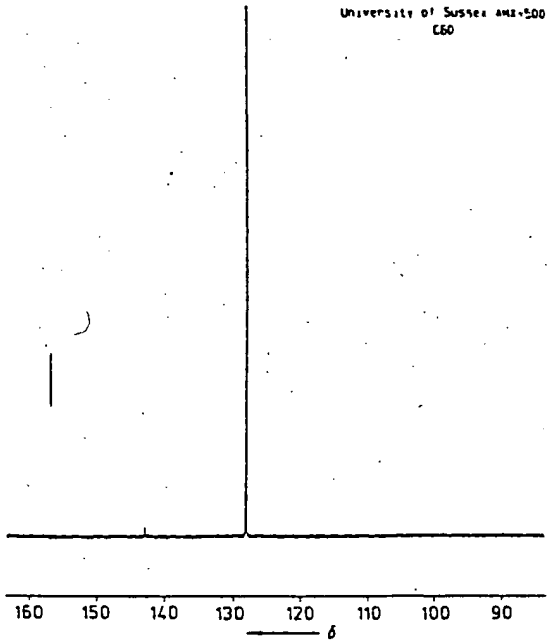

Fig. 27. The first NMR spectrum in which the C_{60} resonance (at $\delta = 143$ ppm) was first identified (barely). The strong line at $\delta = 128$ ppm is (rather appropriately) the resonance of benzene.

us was present. So this was it: a line so small I needed a microscope to see it! Could this insignificant little blip really be the line I had dreamed about for five years? Further work confirmed beautifully that this was the result which we had sought for so long.[52] The joy alleviated almost all the despair I had first felt on reading the paper by Krätschmer et al. One might have thought, as some said, that I should have been pleased to have been proven right when so many had been sceptical. That was not my feeling, probably because I had known ever since the recognition of C_{70} as the second magic fullerene[51] that our structure could not possibly be wrong. I know that my colleagues at Rice University also had no doubts.

What about C_{70}? It turned out to be the icing on the cake, although not without attendent trauma. The wine-red fraction which had masked the pale magenta of C_{60} yielded a mass spectral peak at 840 amu and was clearly C_{70}. According to the expected structure (Fig. 15 right) this compound should exhibit a ^{13}C NMR spectrum with five lines. On Sunday, September 2nd, 1990 I entered the laboratory at the same time as Avent who told me the C_{70} measurement should have just been completed. The spectrum we plotted was sensational—or almost so. There were indeed five lines, but one was in the same position as the C_{60} peak. Could it be that one line was underneath the C_{60} signal? After repeated chromatography to remove the last vestiges of C_{60}, further NMR studies showed the fifth line to be rather different from the others. The resonance of the ten atoms in the waist (Fig. 28c) is more "benzenoid" than the other four resonances.[52] Indeed this line lies dangerously close to the benzene solvent line: had it been a little closer to the benzene signal it would have been swamped and missed altogether. In many ways the five lines of C_{70} are (arguably) more important and significant than the C_{60} singlet. For one thing, they confirm that fullerene carbon atoms are not fluxional; for another, they show that the atoms are not on the perimeter of a monocyclic ring. Both of these cases would lead to a spectrum with a single resonance. Even more important was the fact that the NMR results confirmed the family concept for fullerene cages. It was now clear that a host of stable fullerenes were just waiting to be discovered, as we had long suspected.[53]

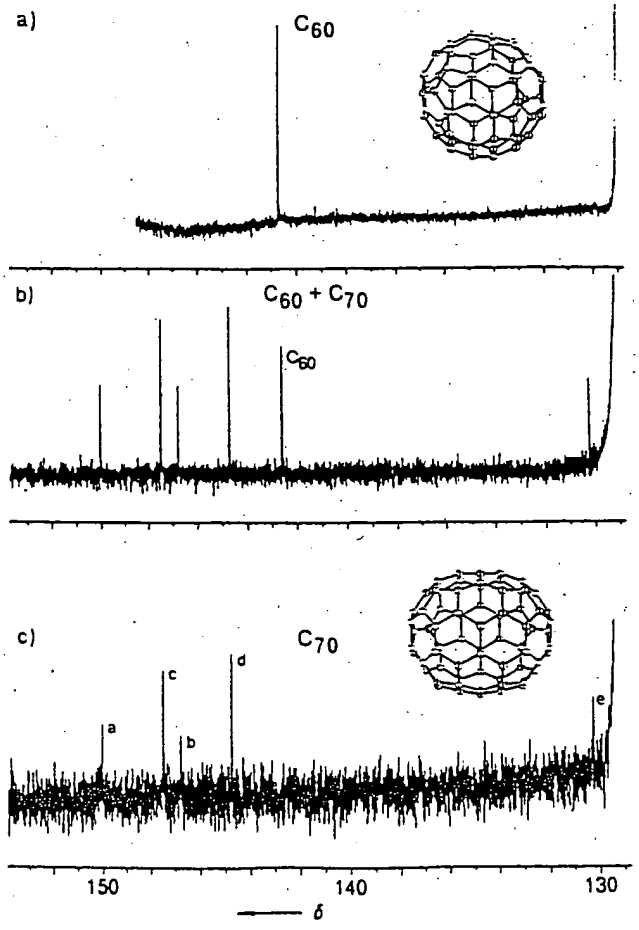

Fig. 28. ^{13}C NMR spectra obtained from chromatographed samples of soluble material extracted from arc-processed graphite: a) spectrum of purified C_{60} (magenta fraction); b) mixed C_{60}/C_{70} sample; c) spectrum of purified C_{70} (red fraction) showing five lines as expected for the symmetric egg-shaped molecule (see Fig. 15).

"The Third Man" is as Elusive as Ever in Space

The elusiveness of C_{60} and my belief that it has been lurking in that blackest of black materials, soot, since time immemorial often reminded me of the role played by Orson Welles in the film "The Third Man". The spirit of this antihero pervades the whole movie although he is seldom seen. Indeed he makes his first appearance late on in the movie in the black shadows of a dark street in Vienna when his face is suddenly illuminated by a light being switched on. For five years C_{60} played a very similar shadowy role—at least as far as I was concerned. My part in the buckminsterfullerene story really started out in space, and this celestial sphere has come down to earth with more of a bounce than a bump; but will it bound back up into space? Is this third form of carbon distributed ubiquitously in space as we surmised the day we found it in the laboratory?[41] Now that we know something about fullerene-60, we should be able to study all its optical properties. It is clear that the UV radiation density in the optically observable interstellar medium is such that the species will be ionized.[73] The possible existence of encapsulated complex ions[73, 74] is quite interesting. However, even with buckminsterfullerene in our hands, we find that this "third man" is as elusive as he ever was in the space between the stars. Perhaps the interstellar form is related to protonated carbon monoxide (HCO^+), which Bill Klemperer identified about 20 years ago.[17] If there are any C_{60} molecules in space there can be little doubt that most will have a proton or some other atom adhering to their surface.[74] $C_{60}H^+$ could probably survive for eons. Other abundant elements, particularly alkali and alkaline-earth metals, must also stick to the surface. Such species will have fascinating optical spectra. For instance, the energy and wavelength of the charge-transfer transition $(C_{60}^+)X \rightarrow (C_{60})X^+$ can be estimated to a first approximation as simply the difference between the ionization potentials of the separated species. For $(C_{60}H)^+$ this transition lies at about 2200 Å. For $(C_{60}Na)^+$ and $(C_{60}K)^+$ the transitions lie in the region of the Diffuse Interstellar Bands[33] and for $(C_{60}Mg)^+$ near zero frequency(!) These observations imply that this and related species will have unusual electrical properties. These processes are probably related to the recently observed superconductivity

of metal-doped fullerene-60 materials.[75] This conjecture is supported by an important new result which comes not from work with bulk material but from cluster-beam studies by McElvaney and Callahan.[76] They found that the gas-phase proton affinity of C_{60} is similar to that of ammonia—a remarkable result! I like to put my trust in intuition: when all else fails it is, after all, our only guide: It is curious to note that some important spectral features of space (the Diffuse Bands) have been visible for decades, yet we do not know what causes them. Now we have discovered that an unexpected molecule, C_{60}, has been under our noses on earth since time immemorial and was invisible until now. It seems to me highly likely that these two observations will turn out to be connected.

Epilogue

Since the time that graphite balloons and C_{60} were twinkles in the eyes of David Jones, Eiji Osawa, and a few other imaginative scientists,[42,43,46-48] there have been many significant contributions, both experimental and theoretical, to the first chapter of the buckminsterfullerene story which has just been completed. These have recently been comprehensively reviewed.[77] Figure 12 shows the Rice/Sussex team and Figure 29, the Sussex Buckaneers. These two teams together with the Heidelberg/Tucson team scored many of the goals in the football match which has just ended. Many new teams have now started to play an exciting, but different, ball game. The important difference is that the players can now see what they are kicking.

Fig. 29. The Sussex Buckaneers football team. From left: Kroto, Abdul-Sada, Taylor, Hare, and Walton.

Apart from the successful observation of the "lone" NMR line, two other matters give me a sense of deep pleasure: one was the beautiful color of C_{60} and, furthermore, that it was seen first at Sussex. The second was that apparently no one else appeared to have followed up the early IR results obtained by the group from Heidelberg and Tucson (September 1989). In retrospect I find this astounding; perhaps it was because the work appeared in the astronomy literature, but more likely it was because research today is carried out under such pressure, and our fear of failure is so great (and exacerbated by funding procedures). Few groups enjoy the luxury of working in the dark—a condition which I feel lies at the heart of true scientific endeavor. I have a videotape of a marvellous BBC documentary on Richard Feynman (the greatest lecturer I had ever heard) from the series "Horizon". In one part he talks on essentially this topic. This 50 minute program had the most profound effect on me. At one point Feynmann described how, when he was hired at Cornell, Bob Wilson had told him that it was the university's responsibility whether he accomplished anything—it was their risk(!) It was not for Feynman to worry about, he should amuse himself. In this way he was freed from the psychological burden of doing anything "important", and he was able to relax and do what he most enjoyed—physics and mathematics—just for the fun of it. How lucky he was. I know of few professional scientists today, certainly no young ones, who are in such a utopian scientific environment. What a sad reflection on today's research, especially since we know in our hearts that human beings achieve most when they are free of pressure. We know that small children learn and discover the joys of nature most efficiently during their play.

News of the breakthroughs spread like wildfire during September 1990, and the method of production developed by the Heidelberg/Tucson group was immediately improved upon[78] at Rice University. As soon as it was known that fullerenes are chromatographically separable and that solution NMR is feasible, other groups confirmed these measurements.[79,80] Don Huffman remarked laconically at a recent symposium, "Everyone is able to repeat these experiments".

A new postbuckminsterfullerene world of round organic chemistry and materials science has been discovered overnight. Almost every day a new paper appears on some novel aspect of fullerene behavior. The group from Rice University has shown that C_{60} forms species such as $C_{60}H_{36}$.[78] Hawkins et al. have made an osmium complex in which the spinning of the fullerene ball is stopped and has enabled accurate bond lengths to be determined.[81] NMR studies by Yannoni et al. have also yielded accurate bond lengths.[82] The radical anion has been polymethylated by Olah's group;[83] platinum complexes have been prepared at DuPont.[84] At AT&T it has been found that the metal-doped material now holds the temperature record for molecular superconductivity.[75] Fascinating differences in the crystal structure of C_{60} have been found which depend upon how the crystals are produced.[77] Foote and co-workers at UCLA have shown that C_{60} transfers light energy efficiently to generate singlet oxygen.[85] Diederich, Whetten, and co-workers have evidence for oxides such as $C_{70}O$.[86] C_{60} is decomposed by light under circumstances which still need to be fully identified.[87] Also interesting is the fact that more fullerenes, such as C_{76} and C_{84}, are being extracted and characterized.[86] The fullerene family has arrived in force, and there are balls of all shapes and sizes for everyone to play with.

This advance is an achievement of fundamental science, not applied science, and serves as a timely reminder that fundamental science can achieve results of importance for strategic and applied areas. The origin of the whole program lay in an interest in aspects of molecular dynamics, allied

with the quest for an understanding of the origin of the carbon chains in space and their possible relationship to circumstellar and interstellar grains as well as soot.[1] These ideas welded together beautifully with the major advance in cluster science brought about by the experimental techniques developed by Smalley and co-workers at Rice University. Krätschmer and Huffman and co-workers were originally motivated by an interest in space dust and, in their recent breakthrough, by astrophysical implications of C_{60}. The C_{60} story has many facets, but more than anything else it is yet another archetypal lesson on the benefits to be gained by supporting pure fundamental science. The field has exploded, and its applications in chemistry and the science of materials are only just starting to be explored. Finally it is worth noting that C_{60} might have been detected 20–40 years ago, perhaps in a sooting flame; one wonders why it took so long.

Another lesson may be learned from these acknowledgements. Important contributions were made in research programs at the University of Sussex (Brighton, UK), the National Research Council (Ottawa, Canada), Rice University (Houston, Texas, USA), the Max-Planck-Institut für Kernphysik (Heidelberg, Germany) and the University of Arizona (Tucson, USA). The discovery of C_{60} is a tribute to not only the international nature of science but also the necessity of interdisciplinary cooperation. The contribution from the University of Sussex to the story started as a consequence of the "Chemistry by Thesis" degree course initiated by Colin Eaborn, which enabled undergraduates (such as Anthony Alexander) to carry out research with supervisors from more than one field. It could only have been successful in the interdisciplinary scientific research and teaching environment which the university pioneered when Sussex was founded in the "optimistic 60s". Sadly this and other courses have been "regulated" out of existence by bureaucrats who have little understanding of how student research expertise is brought to maturity and no awareness of the dire consequences for our future scientific capability. The first part the story could also not have been achieved had chemistry at Sussex been divided into those traditional subsections of organic, inorganic, and physical chemistry. I also had close contacts with astronomers at Sussex, particularly Bill McCrea and Robert Smith. The carbon discoveries resulted from a free-wheeling research program which started with synthetic chemistry (with David Walton, Anthony Alexander, and Colin Kirby) and moved via spectroscopy and quantum mechanics to radioastronomy (with Takeshi Oka, Lorne Avery, Norm Broten, and John MacLeod at the NRC). It moved back to the laboratory and chemical physics (with Jim Heath, Sean O'Brien, Bob Curl, and Rick Smalley at Rice University). In the last phase, key advice came from Michael Jura (an astronomer) which initiated some basic chemistry (with Jonathan Hare, Amit Sarkar, Ala'a Abdul Sada, Roger Taylor, and David Walton). Apart from those mentioned in the text who played direct (and sometimes crucial parts) such as Steve Wood of British Gas, I also acknowledge greatly the help of many others who played indirect parts, particularly graduate students and post-doctoral fellows as well as colleagues such as Tony Stace, Roger Suffolk, and Mike Lappert. Finally I wish to thank Ed Wasserman for some invaluable advice and David Walton in particular for his unfailing help throughout the period of this story and his painstaking assistance in preparing this account.

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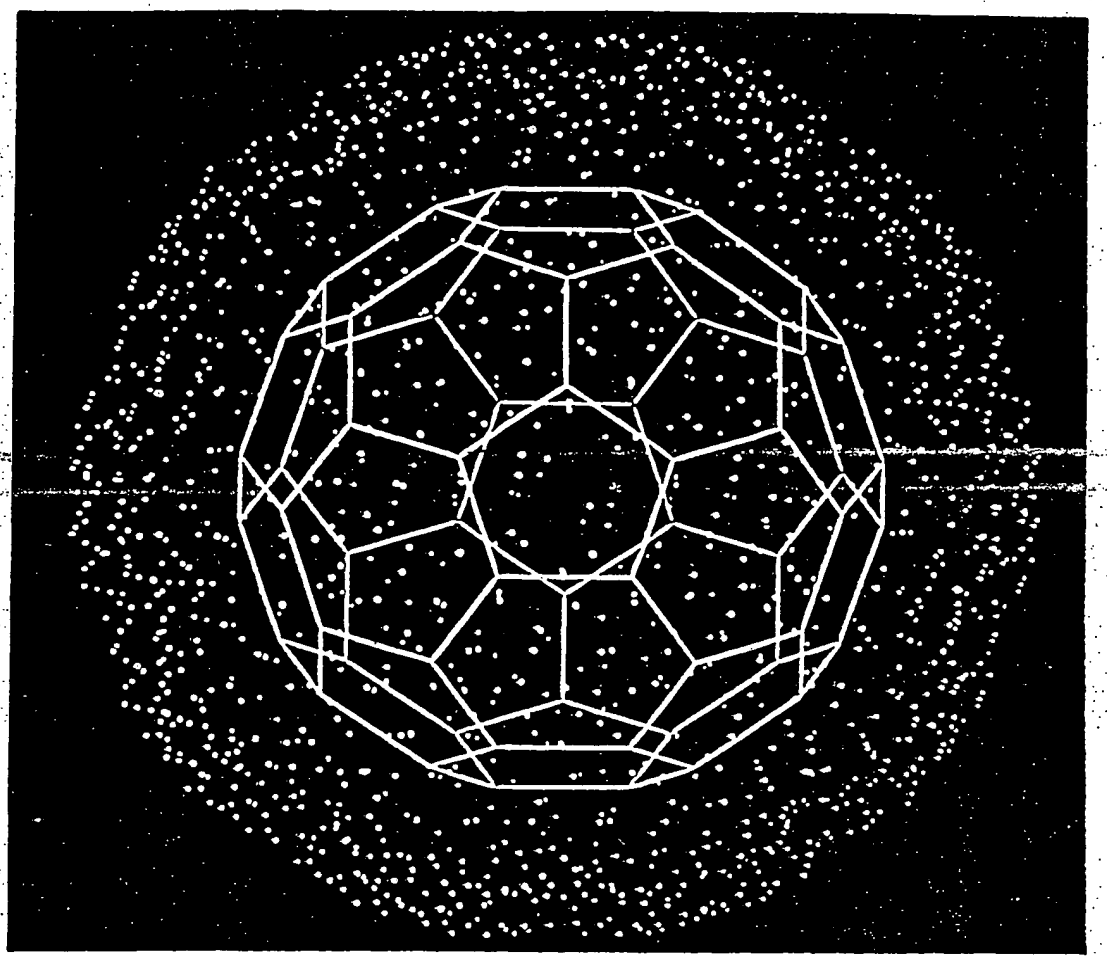

SIXTY-CARBON CLUSTER

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Gordon Thompson
(dimensions of nuclear proliferation)

Jacques Ninio
(origins of life)

Edward Harrison
(steps through the cosmos)

C_{60}: Buckminsterfullerene

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During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously[2-5].

The vaporization of carbon has been studied previously in a very similar apparatus[6]. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the C_{60} peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the C_{60} peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which C_{60} is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38–120 atoms resulted. The C_{60} peak was largest but not dominant. In Fig. 3b, the vaporization laser was fired at the time of maximum helium density; the C_{60} peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C_{70}. In Fig. 3a, the conditions were similar to those in Fig. 3b but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by C_{60}, in fact more than 50% of the total large cluster abundance is accounted for by C_{60}; the C_{70} peak has diminished in relative intensity compared with C_{60}, but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp^2 valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C_{60} molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms[8].

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

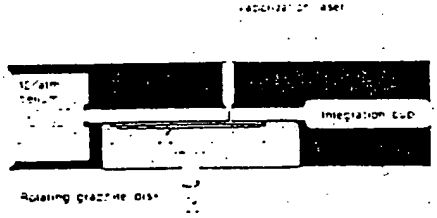

Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam (30–40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle, striking a graphite disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

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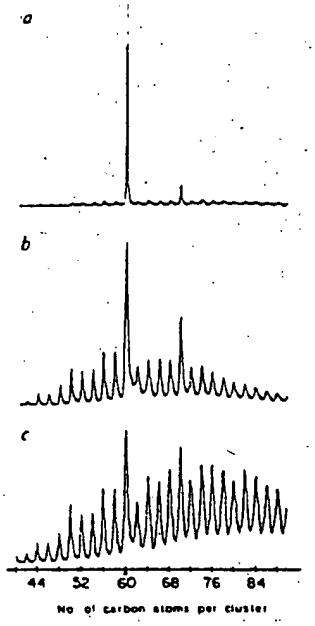

Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In *c*, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in *b* was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in *a* was obtained by maximizing these cluster thermalization and cluster–cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively, C_{60} or a derivative might be the carrier of the diffuse interstellar lines[9].

If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C_{60} derivatives of many kinds—such as C_{60} transition metal compounds, for example, $C_{60}Fe$ or halogenated species like $C_{60}F_{60}$ which might be a super-lubricant. We also have evidence that an atom (such as lanthanum[8] and oxygen[1]) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this C_{60} species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

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Solid C_{60}: a new form of carbon

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A new form of pure, solid carbon has been synthesized consisting of a somewhat disordered hexagonal close packing of soccer-ball-shaped C_{60} molecules. Infrared spectra and X-ray diffraction studies of the molecular packing confirm that the molecules have the anticipated 'fullerene' structure. Mass spectroscopy shows that the C_{70} molecule is present at levels of a few per cent. The solid-state and molecular properties of C_{60} and its possible role in interstellar space can now be studied in detail.

FOLLOWING the observation that even-numbered clusters of carbon atoms in the range C_{30}–C_{100} are present in carbon vapour[1], conditions were found[2–4] for which the C_{60} molecule could be made dominant in the large-mass fraction of vapourized graphite. To explain the stability of the molecule, a model was proposed of an elegant structure in which the carbon atoms are arranged at the 60 vertices of a truncated icosahedron, typified by a soccer ball. The structure, dubbed buckminsterfullerene[2] because of its geodesic nature, has been the subject of several theoretical stability tests[5,6] and has been discussed widely in the literature. Calculations of many physical properties have been made, including electron energies[7–9], the optical spectrum[9], vibrational modes[10–15], and the electric and magnetic properties[16,17]. There has been speculation on the possible chemical and industrial uses of C_{60} (ref. 2), and on its importance in astrophysical environments[18–20]. Until now, it has not been possible to produce sufficient quantities of the material to permit measurement of the physical properties, to test the theoretical calculations, or to evaluate the possible applications.

Some of us have recently reported evidence[21,22] for the presence of the C_{60} molecule in soot condensed from evaporated graphite. The identification was based primarily on the observed isotope shifts of the infrared absorptions when ^{12}C was replaced by ^{13}C, and on comparison of the observed features with theoretical predictions. The measured infrared and ultraviolet absorption bands were superimposed on a rather large continuum background absorption from the graphitic carbon which comprised ≥95% of the sample. Here we report how to extract the carrier of the features from the soot, how to purify it, and evidence that the material obtained is in fact primarily C_{60}.

Method of production

The starting material for our process is pure graphitic carbon soot (referred to below as simply soot) with a few per cent by weight of C_{60} molecules, as described in refs 21, 22. It is produced by evaporating graphite electrodes in an atmosphere of ~100 torr of helium. The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene. The material giving rise to the spectral features attributed to C_{60} dissolves to produce a wine-red to brown liquid, depending on the concentration. The liquid is then separated from the soot and dried using gentle heat, leaving a residue of dark brown to black crystalline material. Other non-polar solvents, such as carbon disulphide and carbon tetrachloride, can also dissolve the material. An alternative con-

FIG. 1 Transmission micrograph of typical crystals of the C_{60} showing thin platelets, rods and stars of hexagonal symmetry.

centration procedure is to heat the soot to 400 °C in a vacuum or in an inert atmosphere, thus subliming the C_{60} out of the soot (W. Schmidt, personal communication). The sublimed coatings are brown to grey, depending on the thickness. The refractive index in the near-infrared and visible is about two. To purify the material, we recommend removing the ubiquitous hydrocarbons before the concentration procedure is applied (for example, by washing the initial soot with ether). Thin films and powder samples of the new material can be handled without special precautions and seem to be stable in air for at least several weeks, although there does seem to be some deterioration with time for reasons that are as yet unclear. The material can be sublimed repeatedly without decomposition. Using the apparatus described, one person can produce of the order of 100 mg of the purified material in a day.

Studies by optical microscopy of the material left after evaporating the benzene show a variety of what appear to be crystals—mainly rods, platelets and star-like flakes. Figure 1 shows a micrograph of such an assemblage. All crystals tend to exhibit six-fold symmetry. In transmitted light they appear red to brown in colour; in reflected light the larger crystals have a metallic appearance whereas the platelets show interference colours. The platelets can be rather thin and are thus ideally suited for electron-diffraction studies in an electron microscope (see the inset in Fig. 3).

Mass spectroscopy

The material has been analysed by mass spectrometry at several facilities. All mass spectra have a strong peak at mass 720 a.m.u., the mass of C_{60}. Significant differences in the spectra occur only at masses lower than 300 a.m.u. Most of these differences seem to originate from the different ionization techniques and in the different methods of desorbing molecules from the sample. Mass spectra recorded at low and high resolution are shown in Fig. 2. The spectra were obtained using a time-of-flight secondary-ion mass spectrometer[23] and a C_{60}-coated stainless-steel plate. In the mass range above 300 a.m.u., the spectrum is dominated by C_{60} ions and its fragments (even-numbered clusters of atomic

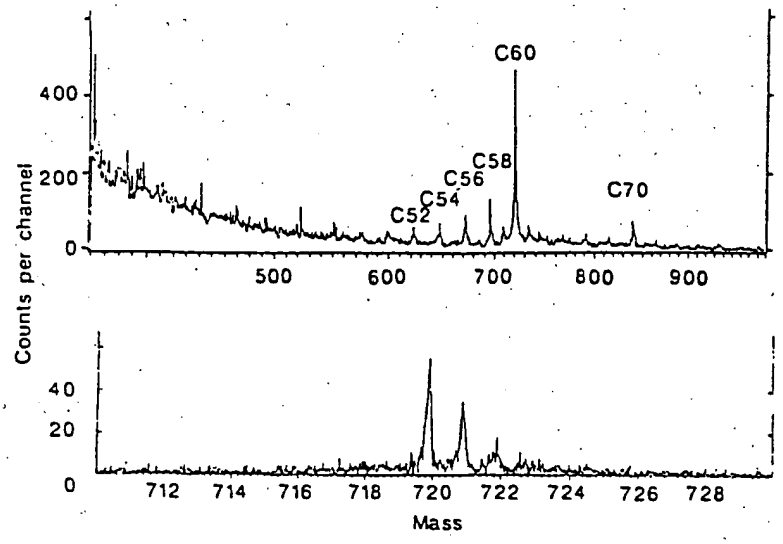

FIG. 2 Low-resolution (top) and high-resolution time-of-flight mass spectra of positive ions obtained from coatings of solid C_{60}. A 5-keV Ar^+ ion beam was used to sputter and ionize the sample. The isotope pattern (bottom) is approximately that expected for C_{60} molecules composed of ^{12}C and ^{13}C isotopes of natural abundance.

~0.1. The high-resolution mass spectrum shows approximately the expected isotope pattern for C_{60}. The increasing background in the low-resolution mass spectrum is not produced by the sample—such backgrounds also occur in blank measurements on uncoated stainless-steel substrates.

So far, the cleanest mass spectra have been obtained when the material was evaporated and ionized in the vapour phase by electrons. In such spectra the low-mass background is substantially reduced and the entire mass spectrum is dominated by C_{60} ions and its fragments. The ratio of C_{70} to C_{60} in these mass spectra is ~0.02 and seems to be smaller than that shown in Fig. 2. Both ratios are of the order of those reported from laser-evaporation experiments[2,3]. We assume, as previously suggested[24], that the C_{70} molecule also has a closed-cage structure, either elongated[24] or nearly spherical[25]. Further details of the mass spectroscopy of the new material will be published elsewhere.

Structure

To determine if the C_{60} molecules form a regular lattice, we performed electron and X-ray diffraction studies on the individual crystals and on the powder. A typical X-ray diffraction pattern of the C_{60} powder is shown in Fig. 3. To aid in comparing the electron diffraction results with the X-ray results we have inset the electron diffraction pattern in Fig. 3. From the hexagonal array of diffraction spots indexed as shown in the figure, a d spacing of 8.7 Å was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The most obvious correspondence between the two types of diffraction is between the peak at 5.01 Å of the X-ray pattern and the (110) spot of the electron diffraction pattern, which gives a spacing of ~5.0 Å. Assuming that the C_{60} molecules are behaving approximately as spheres stacked in a hexagonal close-packed lattice with a c/a ratio of 1.633, d spacings can be calculated. The results are shown in Table 1. The values derived from this interpretation are $a = 10.02$ Å and $c = 16.36$ Å. The nearest-neighbour distance is thus 10.02 Å. For such a crystal structure the density is calculated to be 1.678 g cm^{-3}, which is consistent with the value of 1.65 ± 0.05 g cm^{-3} determined by suspending crystal samples in aqueous $GaCl_3$ solutions of known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions suggest that the order is less than perfect. Further, X-ray diffraction patterns from carefully grown crystals up to 500 μm in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micrometre-sized crystals). It therefore appears that these larger crystals do not exhibit long-range periodicity in all directions.

A likely explanation for these facts lies in the disordered stacking of the molecules in planes normal to the c axis. It is well known that the positions taken by spheres in the third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in a face-centred cubic structure being ABCABC... whereas that in a hexagonal close-

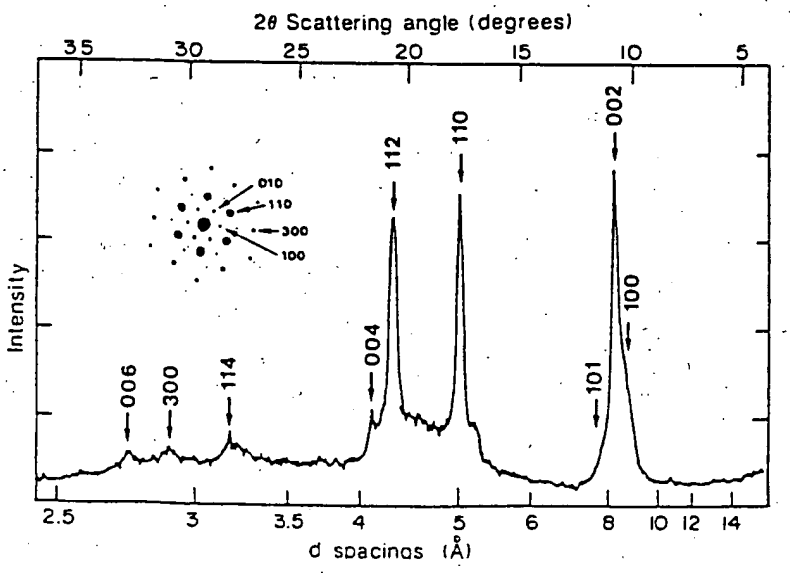

FIG. 3 X-ray diffraction pattern of a microcrystalline powder of C_{60}. Inset (upper left) is a single-crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern. The pattern is from a thin platelet such as those in Fig. 1 with the electron beam perpendicular to the flat face.

TABLE 1 X-ray diffraction results

Measured 2θ (deg)	Measured d spacing (Å)	Calculated d spacing (Å)	Assignment (hkl)
10.2 shoulder	8.7	8.68	(100)
10.81	8.18	8.18	(002)
		7.68	(101)
17.69	5.01	5.01	(110)
20.73	4.28	4.28	(112)
21.63	4.11	4.09	(004)
28.1	3.18	3.17	(114)
30.8	2.90	2.90	(300)
32.7	2.74	2.73	(006)

Assignments for a hexagonal lattice using $a = 10.02$ Å, $c = 16.36$ Å. $(1/d^2) = \frac{4}{3}[(h^2 + hk + k^2)/a^2] + l^2/c^2$.

packed structure is ABABAB . . . If the stacking sequence varies, the X-ray lines owing to certain planes will be broadened by the disorder whereas other lines will remain sharp. Such disordered crystalline behaviour was observed long ago in the hexagonal close-packed structure of cobalt[26-28] where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened by the stacking disorder. Reflections from planes such as (002) remain sharp because these planes have identical spacings in the face-centred cubic and hexagonal close-packed structures. For the planes producing broadened diffraction peaks because of this kind of disorder, the following condition for the Miller indices (*hkl*) has been shown to apply[27,29]: $h - k = 3t \pm 1$ (where t is an integer) and $l \neq 0$. None of these broadened reflections are apparent in the X-ray pattern of Fig. 3. This may explain the weakness of the characteristically strong (101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated C_{70} molecule has yet to be determined.

In small crystals at least, the C_{60} molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, which is entirely consistent with the hypothesis that they are shaped like soccer balls. The excess between the nearest-neighbour distance (10.02 Å) and the diameter calculated for the carbon cage itself (7.1 Å) must represent the effective van der Waals diameter set by the repulsion of the π electron clouds extending outward from each carbon atom. Because the van der Waals diameter of carbon is usually considered to be 3.3–3.4 Å the packing seems a little tighter than one might expect for soccer-ball-shaped C_{60} molecules. The reason for this has not yet been determined.

In summary, our diffraction data imply that the substance isolated is at least partially crystalline. The inferred lattice constants, when interpreted in terms of close-packed icosahedral C_{60}, yield a density consistent with the measured value. Further evidence that the molecules are indeed buckminsterfullerene and that the solid primarily consists of these molecules comes from the spectroscopic results.

Spectroscopy

The absorption spectra of the graphitic soot[21,22] showed evidence for the presence of C_{60} in macroscopic quantities. Following the purification steps described above the material can be studied spectroscopically with the assurance that the spectra are dominated by C_{60}, with some possible effects from C_{70}. Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimation chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of C_{60} smoke (sub-micrometre microcrystalline particles of solid C_{60}) with the particle size depending to some extent on the pressure.

Figure 4 shows the transmission spectrum of an ~2-μm-thick C_{60} coating on a silicon substrate. The infrared bands are at the same positions as previously [21,22] with the

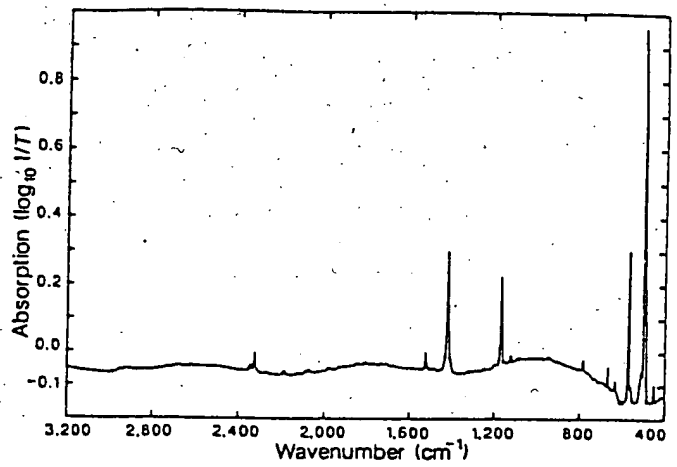

FIG. 4 Infrared absorption spectrum of a coating, ~2 μm thick, of solid C_{60} on a silicon substrate, referenced to a clean silicon substrate. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

intense lines at 1,429, 1,183, 577 and 528 cm^{-1}; here, however, there is no underlying continuum remaining from the soot. In many of our early attempts to obtain pure C_{60}, there was a strong band in the vicinity of 3.0 μm, which is characteristic of a CH-stretching mode. After much effort this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Fig. 4 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities. Vibrational modes to compare with the measured positions of the four strong bands have been calculated by several workers[10-15]. As noted previously, the presence of only four strong bands is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the C_{70} molecule or symmetry-breaking produced (for example) by isotopes other than ^{12}C in the C_{60} molecule or by mutual interaction of the C_{60} molecules in the solid. Weaker features at ~2,330 and 2,190 cm^{-1}, located in the vicinity of the free CO_2 and CO stretching modes, may imply some attachment of the CO_2 or CO to a small fraction of the total number of C_{60} molecules. Another notable feature is the peak at 675 cm^{-1}, which is weak in the thin-film substrates but almost as strong as the four main features in the crystals. We suspect that this vibrational mode may be of solid state rather than molecular origin.

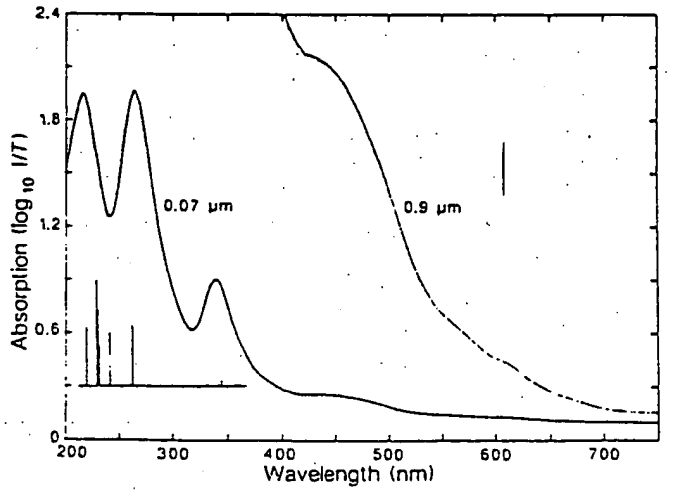

FIG. 5 Visible-ultraviolet absorption spectra of two thicknesses of solid C_{60} on quartz. The calculated[9] positions and relative oscillator strengths for

Figure 5 shows an absorption spectrum taken on a uniform film coated on a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra[22]. Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a plateau between ~460 and 500 nm and a small peak near 625 nm. At the bottom of Fig. 5 we have shown positions and relative oscillator strengths taken from Larsson, Volosov and Rosén[9] calculated for the C_{60} molecule. They also reported a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between our measurements on solid films and the allowed transitions predicted for the molecule. The possibility exists, however, that one or more of the absorption features shown in Fig. 5 are due to C_{70}. We still do not observe a band at 386 nm in our films, as observed[30] using a laser depletion spectroscopy method and attributed to the C_{60} molecule. Quite similar spectra to that in Fig. 5 have been recorded for microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268 and 345 nm.

Possible interstellar dust

The original stimulus for the work[2] that led to the hypothesis of the soccer-ball-shaped C_{60} molecule, buckminsterfullerene, was an interest in certain unexplained features in the absorption and emission spectra of interstellar matter. These include an intense absorption band at 217 nm which has long been attributed to small particles of graphite[31], a group of unidentified interstellar absorption bands in the visible that have defied explanation for more than 70 years[31,32], and several strong emission bands attributed to polycyclic aromatic hydrocarbons[33,34]. Based on the visible and infrared absorption spectra of Figs 4 and 5, we do not see any obvious matches with the interstellar features. The ultraviolet band at 216–219 nm has a similar peak wavelength to an interstellar feature, although the other strong bands of the spectrum have no interstellar counterparts. As the influence of C_{70} absorptions on the spectrum is not yet known, a conclusive comparison with the 217-nm interstellar band is difficult. We note that the visible–ultraviolet spectrum presented here is characteristic of a solid, rather than of free molecules. In addition, these new results do not relate directly to absorption in the free C_{60}^{+} molecular ion, which has been envisaged[19] to explain the diffuse interstellar bands. Nevertheless, these data should now provide guidance for possible infrared detection of the C_{60} molecule, if it is indeed as ubiquitous in the cosmos as some have supposed.

Summary

To our method for producing macroscopic quantities of C_{60}, we have added a method for concentrating it in pure solid form. Analyses including mass spectroscopy, infrared spectroscopy, electron diffraction and X-ray diffraction leave little doubt that we have produced a solid material that apparently has not been reported previously. We call the solid fullerite as a simple extension of the shortened term fullerene, which has been applied to the large cage-shaped molecules typified by buckminsterfullerene (C_{60}). The various physical and chemical properties of C_{60} can now be measured and speculations concerning its potential uses can be tested. □

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at the apple to pick it up, and finally at the box for placement. When the unambiguous instruction was presented in the one-referent context, participants never looked at the incorrect destination (13) (Fig. 1).

In the two-referent context, participants often looked at both apples shortly after hearing "the apple," which reflected the fact that reference could not be established on the basis of just that input. Participants looked at the incorrect referent during 42% of the unambiguous trials and during 61% of the ambiguous trials. [In contrast, in the one-referent context, in which reference could be established given just "the apple," individuals rarely looked at the incorrect object (pencil); this occurred during 0 and 6% of the trials for the ambiguous and unambiguous instructions, respectively.] The time it took participants to establish reference correctly in the two-referent context did not differ for the ambiguous and unambiguous instructions, which indicates that "on the towel" was immediately interpreted as a modifier, not as a destination. Individuals then typically looked directly to the box for object placement without looking at the incorrect destination (Fig. 2). In contrast with the one-referent context, ambiguity in the instruction did not affect the proportion of eye movements to the incorrect destination in the two-referent context (14) (Fig. 3).

Our results demonstrate that in natural contexts, people seek to establish reference with respect to their behavioral goals during the earliest moments of linguistic processing. Moreover, referentially relevant nonlinguistic information immediately affects the manner in which the linguistic input is initially structured. Given these results, approaches to language comprehension that assign a central role to encapsulated linguistic subsystems are unlikely to prove fruitful. More promising are theories by which grammatical constraints are integrated into processing systems that coordinate linguistic and nonlinguistic information as the linguistic input is processed (10, 15). Finally, our results show that with well-defined tasks, eye movements can be used to observe under natural conditions the rapid mental processes that underlie spoken language comprehension. This paradigm can be extended to explore questions on topics ranging from recognition of spoken words to conversational interactions during cooperative problem solving.

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14. The interaction between context and ambiguity for eye movements to the incorrect destination was reliable [$F(1,5) = 8.24$, $P < 0.05$]. Also, a three way interaction between context, ambiguity, and type of incorrect eye movement (to object or to destination) revealed the bias toward a destination interpretation in the one-referent context and toward a modification interpretation in the two-referent context [$F(1,5) = 18.41$, $P < 0.01$].
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TECHNICAL COMMENTS

Origins of Fullerenes in Rocks

Naturally occurring fullerenes have been found in rock samples that were subject to singular geologic events such as lightning strokes (1), wildfires at the K-T boundary (2), and meteoritic impacts (3). These findings are expected, as fullerenes form normally under highly energetic conditions. However, P. R. Buseck *et al.* (4) reported the presence of C_{60} in a carbon-rich rock sample from Shunga, in Karelia, Russia, in which the host geologic unit was highly metamorphosed and there was no evidence of exposure to extreme conditions. If fullerenes did form naturally in such an environment, we would expect them to be widely present elsewhere, and there would be many ramifications. For example, the presence of fullerenes in the earliest times would have implications for the evolution of life (that is, as an early source of large molecules).

We studied the occurrence and distribution of fullerenes in carbon-rich rocks, including samples of shungite from the deposit in Shunga. To avoid sources of contamination by fullerenes, our samples were prepared in laboratories where there had been no previous work done on fullerenes. The outer 2- to 4-mm portion of the shungite samples was removed, and only the core material was gently crushed and ground before mass spectrometry (MS) analysis was carried out directly on the rock powder. Laser Fourier-transform MS and thermal desorption negative ion MS methods were used. In the thermal desorption MS, the temperature was scanned up to 450°C, at which C_{60} and C_{70} are fully volatilized. One sample was purposely contaminated with 100 ppm of commercial fullerenes as a control and to check the sensitivity of the analysis. The result of this reference test indicated that we could detect fullerenes at 10 ppm, or less, without difficulty.

The three samples from the Shunga locality (5) had a variable carbon content of about 100, 90, and 10% by weight. These samples were hosted by about 2-billion-year-old metamorphosed volcanic and sedimentary rocks of the Karelian terrain, which extends northwest through Finland and into Finnmark (northern Norway). We also analyzed one carbon-rich sample from the Bidjovagge mine near Kautokeino, Finnmark, from rocks with broadly similar age, provenance, and metamorphic history as those of Shunga.

To check other geological environments, we analyzed graphite from 3.2-billion-year-old organic carbon-rich shale from a shear zone in the Princeton Mine of the Barberton district, South Africa. Graphite from the Bogala mine, Sri Lanka, was also analyzed (6), a Precambrian sample likely from an inorganic igneous carbon source and formed at temperatures as high as 700°C at 1 to 2 kbar. In contrast, the Princeton Mine sample experienced a maximum temperature of about 300°C.

None of these samples contain detectable amounts of fullerenes. On the basis of these results, we hypothesize that the fullerenes found in the Shunga sample studied by Buseck *et al.* (4) were probably formed by a localized event such as a lightning stroke. This could have happened given the high conductivity of such carbon-rich rocks. Our results and other studies (1–4) appear to show that the formation of fullerenes in nature is limited to highly energetic singular events.

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Response: Finding no fullerenes in several shungite and other samples, Ebbesen *et al.* conclude that the sample we studied (1) was formed by a localized event such as a lightning strike. We find problems with this and other of their observations and interpretations. They state that "there was no evidence of exposure to extreme conditions" for the shungite sample in our study (1). However, we did not discuss occurrence in our report - all we had to study were chips of unknown provenance—and so Ebbesen *et al.*'s conclusion and interpretation seem unsupported. Ebbesen *et al.* also assert that "These findings [origins by lightning, K-T boundary, or meteoritic impact] are expected, as fullerenes form normally under highly energetic conditions." This statement begs the question, as the four terrestrial (1–3) and two extraterrestrial occurrences (4) of natural fullerenes to date tell little about how they form "normally."

We and others (5) have looked at a wide variety of geological samples that contain no detectable fullerenes. The question is—What does this mean? Does it necessarily indicate that only "singular events" can form fullerenes in nature? Also, if fullerenes occur in shungite, then must one conclude they should also "be widely present elsewhere?" Not necessarily.

Aside from the fact that many minerals have been found exclusively in highly limited occurrences, in some cases in only single localities, these questions cannot yet be answered—there are insufficient data. However, there are other mineralogical situations from which, by analogy, one can make at least cautionary guesses.

The biopyriboles provide one example. Although the term was coined over 80 years ago by Johannsen (6), until the late 1970s the only members were the standard mineral groups of micas (biotite), pyroxenes, and amphiboles. At that time, we saw the report of several new biopyribole minerals (7). Initially just curiosities, within a few years the new biopyriboles were reported from several dozen localities worldwide. Chesterite, jimthompsonite, and their mineralogical relatives are now well known and are accepted as widespread albeit minor, rock-forming minerals.

Another example is provided by diamond. Until the 1980s, geologists and solid-state scientists were confident they knew that diamonds form solely at extreme pressures, deep within Earth or, under exceptional conditions, in ultrahigh-pressure experiments that could only be performed in a selected few laboratories. The idea of diamonds being able to form at ambient pressures seemed impossible. Yet today chemical-vapor-deposited (CVD) diamonds, formed at ambient pressures, are almost commonplace (8) in many laboratories, both research and industrial.

The implications, if any, for geological fullerenes are admittedly tenuous. Fullerenes are not prevalent, but we are uncomfortable concluding more than that. We reported that within the shungite they only occur within veinlets. We have confirmed that occurrence in subsequent analyses of the veinlet material in the shungite. Like Ebbesen *et al.*, we wondered whether the shungite fullerenes formed through lightning strikes but, other than the fullerenes themselves, there is no evidence on how they formed.

On the basis of laboratory data, we know that optimal fullerene growth occurs in gas-phase reactions (9), and such conditions might occur during the multiple strokes of lightning (3). Indeed, lightning might explain the origin of the fullerene-bearing veinlets in the shungite, but it would be highly fortuitous if we would have inadvertantly chanced on such unusual samples. There are other references to the occurrence of fullerenes in shungite (10), but details are lacking about where in the shungite the fullerenes occur or in which samples.

There is abundant evidence that the mineralogical world is wondrously complex and full of surprises. We prefer to remain an open mind about the extent of fullerene occurrences in the geological environment than to make possibly premature conclusions based on the limited data at hand.

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CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

I hereby certify that this DECLARATION OF HAROLD W. KROTO UNDER 37 C.F.R. §1.132 is being deposited with the United States Postal Services as first class mail in an envelope addressed to: Box interference, Assistant Commissioner for Patents, Washington D.C. on July 31, 1995.

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I hereby certify that a true copy of this DECLARATION OF HAROLD W. KROTO UNDER 37 C.F.R. §1.132 has been served upon Eugene O. Palazzo, attorney for the junior parties, Ziolo, Mort et al. and Ziolo, by mailing a copy thereof by first class mail, postage prepared, to him at his address of record.

Dated: July 31, 1995

Stephen D. Murphy

Materials Science Abounds at the 1993 MRS Fall Meeting

Wolfgang Krätschmer (left), professor at the Max-Planck-Institute für Kernphysik, and Donald R. Huffman, professor in the Department of Physics at the University of Arizona display their 1993 Medals Awards "for the discovery of a way to produce macroscopic quantities of the fullerenes and for elucidating many of their physical and chemical properties."

The 1993 MRS Fall Meeting in Boston brought with it a celebration of the Materials Research Society's 20th anniversary. In addition to the technical symposia coordinated by meeting chairs Philippe M. Fauchet (University of Rochester), David B. Poker (Oak Ridge National Laboratory), and Alan L. Taub (Ford Research Laboratory), the meeting offered a glimpse into the history of MRS and the development of materials science over the past two decades. The meeting, held November 29 through December 3 and attracting an estimated 3,800 attendees, was embellished with a photo display showing the chronology of MRS events, plus introductory historical remarks kicking off some of the technical symposia.

Symposium AA, designated the Balluffi Fest, also celebrated past accomplishments. It was a tribute to the progress in understanding atomic-scale imperfections, in honor of Robert W. Balluffi's exemplary career.

The meeting was also a time for looking into the materials research "crystal ball." A panel discussion in Symposium A, Materials Synthesis and Processing Using Ion Beams, looked at prospects for new commercial processes and applications of ion beams for cutting tools, aircraft parts, silicon-on-insulator (SOI) processing, and others.

In another session, Tom Seidel, chief scientist at Sematech, and Tadahiro Ohmi, Tohoku University, described the status of the semiconductor industry and where it's headed, including prospects for SOI technology and wide bandgap materials. Ohmi described the aim for human intelligence systems; current technology achieves the equivalent of 10^3 neurons, still a far cry from the human brain's 10^{10} neurons.

A panel discussion during the Symposium on the Scientific Basis for Nuclear Waste Management examined the objectives and limitations of scientific studies for determining appropriate management of nuclear waste. Panelists acknowledged that there are diverse views about what scientific solution is optimum. They neared consensus, however, on the need to incorporate flexibility in a system, so the system can be altered based on subsequent research findings. Panelists were also of the opinion that the government's expectation of 10,000-year predictions is a major impediment to the institution of any system.

Symposium I, Developing Materials Processes for Factories, addressed manufacturing issues in materials science. It was led off by NSF Director, John H. Hopps, who spoke about the Clinton administration's role in manufacturing. Other sessions presented examples of process development in a variety of materials classes.

Biology continued its growing link with materials science. Bioelectronics, particularly bacteriorhodopsin, was the subject of an intense session. This material has properties that are highly favorable for applications such as optical data storage and holographic pattern recognition.

The first MRS symposium on New Materials for Advanced Solid State Lasers, Symposium R, revealed rapid progress over the past five years. Research has focused on the elements of miniaturization, cost reduction, and wavelength selectivity.

The diversity of topics in Symposium Q on Organic Solid State Materials demonstrated the long-term significance and ever-changing nature of the field. Liquid crystals are well-established commercially, while light-emitting organic polymer diodes are just emerging; yet both are potentially useful in commercial development of flat panel displays.

Characterization techniques have further been refined. New microscopy and spectroscopy techniques are directly revealing physical properties down to nanometer and molecular levels, and in some cases even below 1 angstrom. Non-invasive optical diagnostic techniques have been developed for monitoring materials and process properties.

Defects, interfaces, and phase transformations received attention in several symposia. Issues related to thin oxides for MOS devices, formation and properties of iron silicides, metal reactions with Si-Ge alloys; and defect states common to a variety of amorphous materials as they recrystallize.

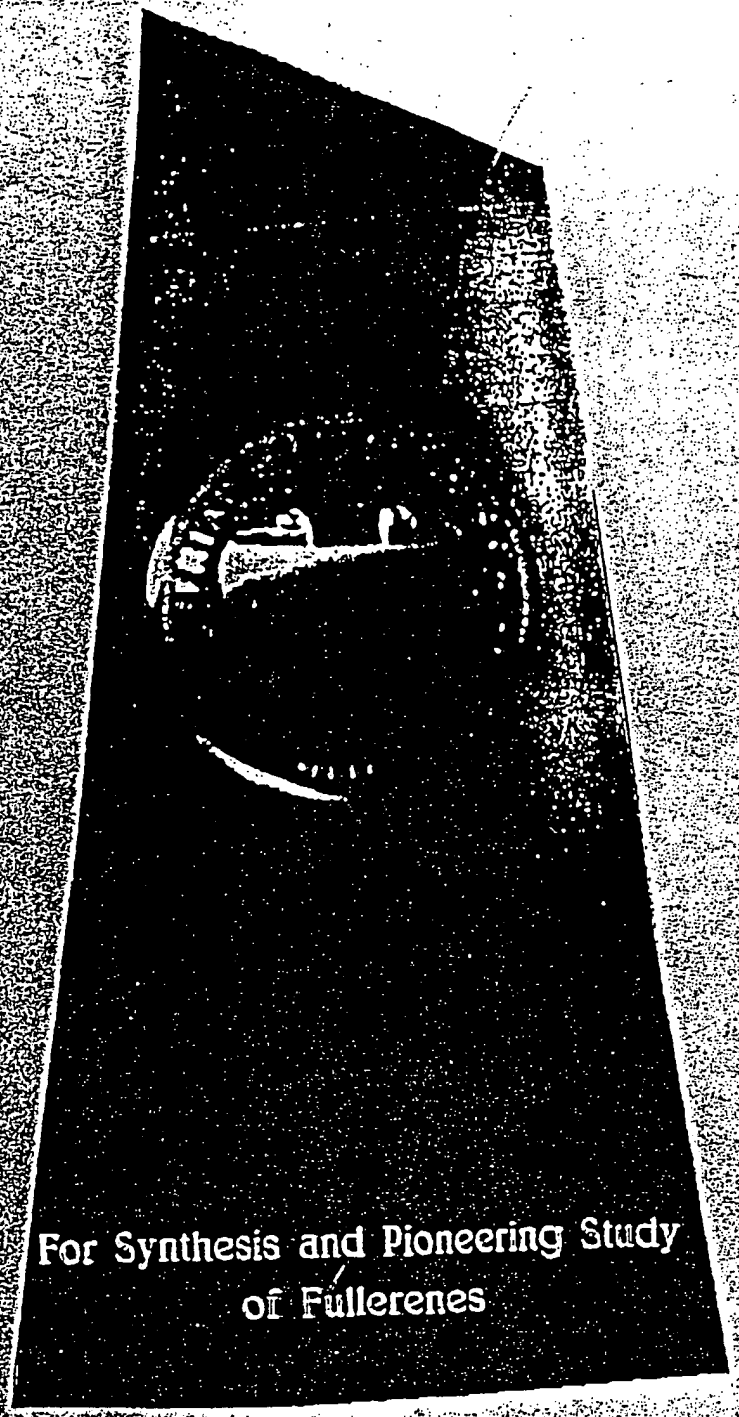
In the symposium on Superconductors, a particular emphasis on high-power applications of high-temperature superconductors revealed progress in creating longer wire lengths, higher current carrying capacity, and larger coils.

Other symposia covered fullerenes, electronic packaging, advanced semiconductors and heterostructures, complex fluids, disordered materials, non-oxide covalent ceramics, MOCVD, gas-phase surface chemistry, and high-temperature silicides and refractory alloys.

For highlights of the symposia, read the summaries on the following pages. More detailed information is available in the published proceedings.

Plenary Session

Hazel O'Leary, the Department of Energy Secretary, drew an overflowing crowd of about 800 people. She spoke about DOE's role in support of materials research, and how science and technology can be used as a strategic weapon in the new "economic war." See Material Matters, p. 7–13, in this issue for her plenary address.



Xerox "Copy" of the Materials Research Society Award with embedded Gold Medallion.

"For Synthesis and Pioneering Study of Fullerenes"

CERTIFICATE

The EUROPEAN PHYSICAL SOCIETY certifies hereby that the
1994 HEWLETT-PACKARD EUROPHYSICS PRIZE
for Outstanding Achievement in Solid State Physics
has been awarded to

Donald R. HUFFMAN
Wolfgang KRÄTSCHMER
Harold W. KROTO
Richard E. SMALLEY

for the Discovery of New Molecular Forms of Carbon
and their Production in the Solid State

Madrid, 30 March 1994

The President:

Norbert Kroo
N. Kroo

The Secretary:

Andrea Taroni
A. Taroni

EUROPEAN PHYSICAL SOCIETY

CITATION

Donald R. Huffman
Wolfgang Krätschmer
Harold W. Kroto
Richard E. Smalley

The Hewlett-Packard Europhysics Prize of the European Physical Society
for
Outstanding Achievements in Condensed Matter Physics for the year 1994
is awarded to you in recognition of your

"DISCOVERY OF NEW MOLECULAR FORMS OF CARBON AND THEIR PRODUCTION IN THE SOLID STATE".

Until recently, the only known forms of pure crystalline carbon were diamond and graphite. You have discovered a third form of carbon in which, by inclusion of pentagonal rings, graphite-like sheets are wrapped into cage molecules, so-called fullerenes.

Using laser evaporation combined with supersonic-beam mass spectroscopy, Richard Smalley and Harold Kroto discovered single fullerene molecules, in particular the archetype C_{60}. Kroto and Smalley were able to foresee the shape of C_{60} as being that of a truncated icosahedron, a soccer-ball, and they predicted the existence and the structural principle of the fullerenes. Wolfgang Krätschmer and Donald Huffman found that, under certain conditions, C_{60} is abundant in soot produced by a carbon arc and cooled by helium. They could dissolve C_{60} (and C_{70}) out of the soot, produce crystals, and verify the predicted soccer-ball structure.

The Krätschmer-Huffman method has prompted widespread research on applications of fullerenes. So-far, fullerenes have been engineered with surprising superconducting, optical, mechanical, and chemical properties.

You have found a third, form of pure carbon whose rôle in nature we are just beginning to understand, and whose potential for technological applications is being intensively investigated. In recognition of these achievements, you have been awarded the Hewlett-Packard Europhysics Prize for 1994.

Madrid, 30 March 1994

The Selection Committee

question of going beyond the that Nature has imposed for the maxi... size of nuclei. The relative occurrence of prolate versus oblate shapes is a non-trivial issue that has been discussed a good deal in nuclear physics. Semi-classical theory offers a rather transparent model description of this in terms of the response of triangular and other closed classical orbits to deformation, but the problem is that one needs larger Fermi droplets than nuclear physics can provide to test the theory.

Fission

The break-up of a drop of quantum liquid under the influence of its electric charge, *i.e.*, fission, can be studied from a new angle by examining the fission of multiply charged metallic clusters. In all cases the fission process depends on the competition between the cohesive surface force and the repulsive electrical force. The relevant parameter is therefore the ratio of the Coulomb energy to (two times) the surface energy of a sphere, *i.e.*,

$$E_c/2E_{surf} = (Q^2/N)/(Q^2/N)_{crit}$$

where Q is the charge. Inserting typical material constants into the equation one realizes that while 200 nucleons can hold 90 elementary charges together, the same number of metal atoms can hold at most 9 excess charges without immediately fissioning. This reflects the difference between nuclear cohesion, which is due to the strong force, and metallic cohesion which is of electromagnetic origin.

A new stage is set for fission studies thanks to this difference. Quantum effects are likely to be much more pronounced in metallic clusters than in nuclei (modifications of the smooth liquid-drop picture owing to quantum effects at the fission-like saddle-point shape makes fission interesting already in nuclei). There are some intriguing experimental results for the fission of doubly charged silver and potassium clusters [13] with sizes up to $N = 30$. The division into different fragment pairs seems indeed to be dominated by quantum effects for symmetric mass splits. For clusters in this size range one expects the saddle shapes to be (nearly) two spheres in contact, so the quantum effects are those relating to spherical shapes. Since these shapes can be studied by other means, it would be even more interesting to investigate, using new experiments, the fission of larger clusters with charges greater than 2 since they can have saddle shapes that do not resemble two spheres in contact.

Atypical Molecules: A Bridge to Chemistry

The cooling of a hot metallic droplet through evaporation of (neutral) atoms has much in common with neutron evaporation from the compound nucleus. In both cases the process is described by transition-state theory. The difference lies in the level-density laws. For nuclei, the level-density law of a fermion system alone applies, while for a metal cluster the level density is a product of the ionic, *i.e.*, the oscillator level density, and the fermionic electron level densities. It is the latter that is strongly modulated by the cluster's shell structure, so the fermionic structure plays an important rôle in evaporation processes involving clusters, and in describing how shell structure becomes washed out with increasing temperature. There exists here a bridge to transition-state theory in chemistry, where the emphasis lies on the oscillator level density, while the electrons are assumed not to contribute because they presumably remain in their adiabatic ground state during typical molecular dissociation processes. In this sense, metal clusters are atypical molecules. Once again we see how a marriage between the young science of cluster physics and a more mature partner can be rich in mutual inspiration.

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1994 HEWLETT-PACKARD EUROPHYSICS PRIZE

New Molecular Forms of Carbon

The 1994 Hewlett-Packard Europhysics Prize of EPS for outstanding achievements in condensed matter physics has been awarded for "the discovery of new molecular forms of carbon and their production in the solid state" to D.R. Huffman (The University of Arizona, Tucson, USA), W. Krätschmer (Max-Planck Institut für Kernphysik, Heidelberg, Germany), H. Kroto (University of Sussex, UK), and R.E. Smalley (Rice University, Houston, USA).

Donald Huffman was honoured last year for the discovery of C_{60} by being appointed the Regents' Professor of Physics in the Department of Physics, The University of Arizona, Tucson, Arizona, USA. He studied at Texas A&M University and at Rice University before receiving his Ph.D. from the University of California, Riverside, in 1966. After working as a National Science Foundation postdoc at the University of Frankfurt, he joined The University of Arizona as an Assistant Professor in 1968, becoming Professor in 1975. Professor Huffman, whose research focuses on the optical properties of small particles, has visited Europe regularly, first as a Visiting Scholar to the University College, Cardiff, and then on a sabbatical to the European Space Agency operations in Noordwijk and as

Clockwise from the upper left: D.R. Huffman, W. Krätschmer, R.E. Smalley, and H. Kroto.

a Humboldt Senior US Scientist to the Max Planck Institute in Stuttgart an idelberg. After filing a patent application ...i the C_{60} production process, which is handled by Research Corporation Technologies, he set up the first commercial operation to manufacture and market the material, and was appointed in 1991 to be the first Director of the newly formed Arizona Fullerene Corporation, which aims to bring together fullerene research carried out at The University of Arizona and Arizona State University. Professor Huffman won the Materials Research Society's 1993 MRS Medal for his work on fullerenes.

Wolfgang Krätschmer has been with the research staff of the Max Planck Institute for Nuclear Physics, Heidelberg, since 1976, and has acted since 1987 as a Co-investigator for the development of a photospectrometer for the European Space Agency's orbiting infrared observatory ISO. He studied physics at the TU Berlin and received his doctorate from the University of Heidelberg in 1971 for research on radiation damage carried out at the Max Planck. Dr. Krätschmer's research from 1971 to 1977 mainly concerned heavy-ion astrophysics and after working for a year on interstellar silicate materials with D.R. Huffman at the University of Arizona and with R.F. Knacke at Stony Brook, he began studying astrophysically important dust materials. In recognition of the discovery of fullerenes, he was awarded the German Physical Society's 1992 Stern Gerlach Prize for Physics, the Deutschen Forschungsgemeinschaft's 1993 Leibniz Prize, and the 1993 Alexander von Humboldt Prize.

Harold Kroto has been the Royal Society Research Professor in the School of Chemistry and Molecular Sciences, The University of Sussex, Brighton since 1991. He studied chemistry at the University of Sheffield where he stayed on to complete his Ph.D in 1964 before working as a postdoc with the National Research Council in Ottawa, Canada, and as a member of the technical staff of the Bell Telephone Laboratories, Murray Hill, USA, for one year. In 1967, he joined the University of Sussex as a Tutorial Fellow, becoming Professor in 1985. Professor Kroto, whose research interests mainly involve interstellar molecules and circumstellar dust and the spectroscopy of unstable chemical species, has spent time as a visiting scientist or professor in Vancouver, Ottawa, Berkeley, Zagreb, Paris, and Los Angeles. He became a Fellow of the Royal Society in 1990 and for work on fullerenes, was awarded the American Physical Society's International Prize for New Materials (jointly with R.F. Curl and R.E. Smalley), the 1992 Italgas Prize for Chemistry and the Royal Society of Chemistry's 1993 Longstaff Medal. Aside from serving on committees belonging to the UK's Science Research Council, the Science and Engineering Research Council, the International Astronomical Union, and the Max Born Institute, he has been a member of the Editorial Board of *Chem. Soc. Reviews* since 1986, of *Z. Physik D* since 1992, and of *J. Chem. Soc. Chem. Comm.* since 1993.

Richard Smalley has been the Gene and Norman Hackerman Professor of Chemistry at Rice University, Houston, Texas, USA, since 1982, and Professor of Physics since 1992. Educated at Hope College and The University of Michigan, he worked as a research chemist with Shell for four years before taking a M.A. and a Ph.D. in chemical physics (in 1973) from Princeton University. After spending four years as a postdoc at The University of Chicago where he pioneered supersonic jet laser-beam spectroscopy, he returned to Princeton as an Assistant Professor in chemistry in 1976, becoming Professor in 1981. Professor Smalley, whose research interests mainly involve spectroscopic studies of gases, molecules, radicals, ions, and simple clusters, has won several prizes for C_{60} research including the 1991 Irving Langmuir Prize in Chemical Physics, the 1991 *Popular Science Magazine* Grand Award, the 1992 Robert A. Welch Award in Chemistry, the 1992 American Physical Society's International Prize for New Materials (jointly with R.F. Curl and H. Kroto), the US Department of Energy's 1992 E.O. Lawrence Award, the 1993 John Scott Award, and the 1993 William H. Nichols Medal. He is a member of the APS and the American Chemical Society and has been on the Editorial Boards of *Chem. Phys. Lett.* since 1982, of *J. Cluster Sci.* since 1988, and of *Molecular Phys.* since 1991.

CALL F NOMINATIONS

1995 Hewlett-Packard Europhysics Prize

The Selection Committee for the Hewlett-Packard Europhysics Prize invites nominations for the 1995 award. The Prize is give for an outstanding contribution to condensed matter physics within the previous five years, with the potential for leading advances in electronic, electrical or materials engineering. Nominations may be submitted by EPS members as individuals or as representatives of a Division, Section or Group.

Previous winners have been B.L. Altshuler, A.G. Aronov, D.E. Khmelnitskii, A.L. Larkin, and B.Z. Spivak (1993) and H. Ibach, G. Ertl and J.P. Toennies (1992). To maintain the extremely high standard, it is necessary that the Committee receives proposals which represent the breadth and strength of European condensed matter physics. Proposals should indicate the motivation for the award and include, if possible, a brief *curriculum vitae* of each of the nominees and a short list of major publications. Letters of support from authorities in the field which outline the importance of the work are also very helpful.

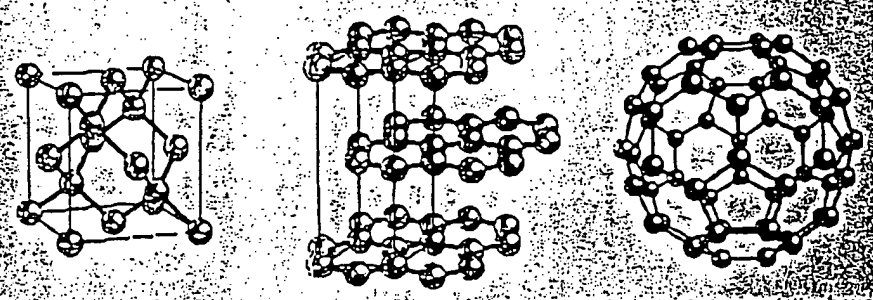
All information will be treated as strictly confidential, and although proposals are acknowledged, there will be no further correspondence. Nominations should be submitted before 30 June 1994 to the Selection Committee, H.-P. Europhysics Prize, EPS, P.O. Box 69, CH-1213 Petit-Lancy 2.

Fullerenes: The Classical Profile of a Major Scientific Breakthrough

Until recently, the only known forms of pure crystalline carbon were diamond and graphite. In diamond, each carbon atom is tied to four others in a three-dimensional tetrahedral arrangement by strong sp^3 bonds. The result is a transparent insulator of unique hardness. In graphite the atoms lie in two-dimensional sheets of hexagons, like chicken-wire, with each atom tied to three others by strong sp^2 bonds. The fourth electron occupies a π bond formed from the perpendicular p-orbitals and this lies at the origin of the black colour and electrical conductivity. The sheets sit in stacks which makes graphite a good lubricant.

The prizewinners discovered a third form of carbon in which graphite-like sheets are wrapped into cage-like molecules, so-called fullerenes named after the American engineer Buckminster Fuller who constructed geodesic domes according to similar principles. The way in which chicken wire may be given curvature is by mixing pentagons between the hexagons and, as shown by Euler, with 12 pentagons the cage closes, the number of hexagons determines the size of the cage. Finally, three-dimensional packings of cage molecules yield solids, the so-called fullerites.

The archetype molecule and the first one discovered is C_{60}, the "buckyball", which has the shape of a football and a diameter of 0.7 nm (a real football usually has its 12 pentagons painted black and its 20 hexagons white). C_{60} is the smallest fullerene in which the 12 pentagons are kept apart by hexagons. The edge between a pentagon and a hexagon in C_{60} is a sp^2 bond, and the edge between two hexagons carries an additional π bond, that is, the former edge is a single



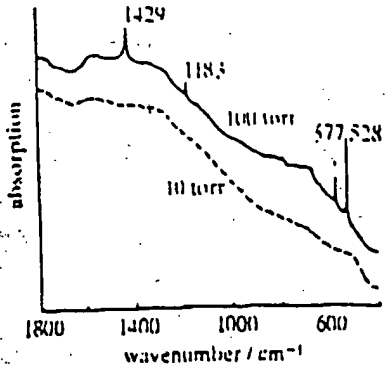
Basic structures of carbon crystals: from the left, the tetrahedral network of diamond, the hexagonal layers of graphite, and the buckyballs of fullerite.

bond and the latter a double br These features give the C_{60} molecule gre strength and make the solid a yellowish semiconductor. In solid C_{60}, the molecules are positioned on a face-centered cubic lattice with a closest approach between balls nearly the same as the distance between the sheets in graphite. At normal pressures, the solid is therefore soft, like graphite, but becomes extremely hard at high pressures. Thrown against steel walls at speeds of about twenty thousand miles per hour, solid C_{60} just bounces back.

The C_{60} molecule has the shape of a truncated icosahedron as constructed by Archimedes; its point symmetry is the highest possible, after that of a perfect sphere. With the addition of 5 more hexagons, a belt of hexagons forms around the molecule, which then attains the shape of an American football. This C_{70} was the second fullerene discovered by the prizewinners.

Interstellar Matter Suggested New Form

What led to the discovery of the fullerenes and fullerites was not the search for new lightweight materials with superb mechanical, electrical, magnetic, or optical properties, nor was it the search for new catalysts, batteries or pharmaceuticals, but the search for the composition and structure of interstellar matter. Huffman and Krätschmer had been trying for years in their respective laboratories to produce a carbon dust which had the same absorption spectra as observed for interstellar dust. Together in Heidelberg in 1983 they evaporated graphite rods by resistive heating in a helium atmosphere and noted that a double hump in the ultraviolet absorption spectrum of the soot which they had never encountered before appeared at a particular helium pressure.



Absorption of carbon particles in the infrared. At elevated helium quenching gas pressure, there are four stronger lines emerging out of the continuum. Theory predicts precisely four ir-active fundamentals for a football structured C_{60} molecule and they should occur close to the measured positions. Such spectra gave the first strong hint that C_{60} had been produced in macroscopic quantities. Some of the tiny line features originate from the less abundant fullerene C_{70}.

H. Kroto and D. Walton in Brighton had been interested for over 10 years in certain interstellar molecules containing long, straight carbon chains and, together with radioastronomers, had succeeded in verifying the presence of such chains with up to nine atoms. However, they believed that much longer chains might be formed in the outer atmosphere of red giants. In 1984, Kroto heard from his friend R.F. Curl about an apparatus designed by R.E. Smalley and his students in Houston whereby laser evaporation combined with a supersonic jet of inert gas produced a beam of atom clusters, whose sizes were analyzed by mass spectroscopy. Kroto and Curl succeeded in talking Smalley into trying out carbon. The chains being sought for were found, but the attention of Smalley, Kroto, Curl, and of their students J.R. Heath and S.C. O'Brien, was drawn to larger clusters, notably to C_{60} which under particular conditions turned out to be much more abundant than all the others. Smalley and Kroto, who apparently knew more about Buckminster Fuller's domes than the shape of a football, were able to guess the structure, as well as the structural principles of other fullerenes. During the next years they gathered considerable circumstantial evidence to support their hypothesis. Also carried out were theoretical calculations of the physical properties of this icosahedral molecule, such as the ultraviolet absorption and the infrared vibration spectra, but for five years nobody was able to produce C_{60} in the quantities needed for a structural determination.

Bulk Production Led to Confirmation

At about this time, Huffman started wondering whether the double hump he and Krätschmer had seen might have been caused by C_{60}. In 1989, Krätschmer and his students B. Wagner and K. Fostiropoulos reproduced the results of the 1983 carbon-arc experiment and furthermore measured the mass spectrum and the infrared vibrational spectrum (see figure), which was predicted to exhibit only four peaks due to the icosahedral symmetry of the molecule. Surprisingly, these were the vibrations of the soot samples produced under double-hump conditions; C_{60} thus seemed to be present in abundance. Substitution of ^{12}C by the heavier isotope ^{13}C produced the shift of the vibrational spectrum expected for an all-carbon molecule. Finally, the Heidelberg group did what a chemist would have done right away: they tried to dissolve the sample in benzene, which should work if the soot really did contain "spherical benzene". When they saw the solvent turn red, the group knew that it had produced the first concentrated solution of fullerenes. The solvent was evaporated and it was found that tiny crystals remained, which readily redissolved. The crystals could be sublimed and condensed to form smooth films which later turned out to contain about 80% C_{60} and 20% C_{70}. Huffman and his collaborator L. Lamb in Tucson could immediately verify Krätschmer's findings and were able to study the crystal structure of C_{60} using X-ray and electron diffraction. Kroto in Brighton had tried the Krätschmer-Huffman method two years earlier, but ran out of funding. He and his students now returned to the technique and succeeded in producing a C_{60}-C_{70} solution, in separating the two molecules, and in proving their structures by ^{13}C nuclear magnetic resonance.

O.K. Andersen
MPI für Festkörperphysik, Stuttgart

Potential Applications Abound

Research on applications of fullerenes has spread like wildfire since the discovery in 1990 by Krätschmer and Huffman of a simple way to produce these novel molecules. Within months, many groups could make their own fullerenes. One group looked with the electron microscope not at the carbon soot but at the burned ends of the graphite rods used in the evaporation process and found "chicken wire" rolled up like tobacco leaves in a cigar. Another found shells of successively larger fullerenes resembling onion rings. It has been possible to make from the rolls "buckytubes" several nm in diameter and up to 1000 times longer. The hexagons spiral their way along the tube until reaching the end, where the presence of 6 pentagons ensures a proper capping with no bonds left dangling. It has even been possible to open the tubes and through some kind of capillary effect to fill them with lead atoms. The buckytubes could be the strongest fibers known and may even find use as microscopic wires.

It has been found that semiconducting solid C_{60} can be doped with alkali atoms entering between the buckyballs and one of the first surprises in fullerene research was that K_3C_{60} becomes superconducting below 19 K (the highest transition temperature obtained in a fullerene is presently 33 K). Another surprise was that intercalation of an organic agent (TDAE) in solid C_{60} produces a soft ferromagnet. Highly ordered C_{60} films can be grown on crystalline substrates such as gallium arsenide and this property may make such films suitable for microelectronic fabrication. Researchers have claimed that putting a thin layer of C_{70} on a silicon surface can speed up the growth of diamond films by ten orders of magnitude. Such films could harden tool surfaces, or be used to insulate microelectronic circuits. Films containing C_{60} and C_{70} have the interesting property that they become more opaque in bright light and might therefore find use as optical limiters. Adding C_{60} and C_{70} to certain polymers yields excellent photoconductors. Hexagons in some of the larger fullerenes form a spiral instead of a belt resulting in non-linear optical properties. Such materials might find applications in the higher-harmonic generation of light.

Fullerenes were originally thought to be so stable that they should not react with other materials. But chemists have learnt how to slip an extra carbon or nitrogen atom into a fullerene as a hitching post for new ingredients, thus creating the "bunnyball". This opens the way for making complex compounds based on fullerenes, called fulleroids. Decorating fullerenes with transition metal complexes may result in excellent catalysts, while "Teflon balls" ($C_{60}F_{60}$) have been produced in macroscopic quantities and might turn out to be an excellent lubricant. Such tiny ball bearings would also fit nicely into the new world of "micro-machines". Finally, fullerene cages have been used to trap various atoms. In this form, the fullerenes could perhaps find application in molecular batteries and in drug-delivery systems.

The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"

Press release

The Fullerene Gallery

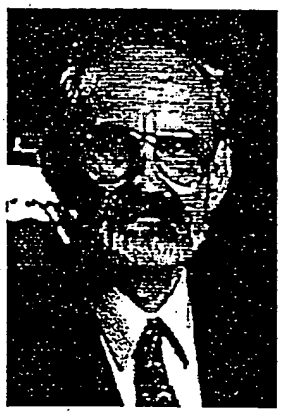
Robert F. Curl, Jr.

USA

Rice University
Houston, USA

1933 -

Autobiography



Sir Harold W. Kroto

U.K.

University of Sussex,
Brighton, U.K.

1939 -

Autobiography

Richard E. Smalley

USA

Rice University,
Houston, USA

1943 -

Autobiography

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Press Release: The 1996 Nobel Prize in Chemistry

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

9 October 1996

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor **Robert F. Curl, Jr.**, Rice University, Houston, USA,
Professor **Sir Harold W. Kroto**, University of Sussex, Brighton, U.K., and
Professor **Richard E. Smalley**, Rice University, Houston, USA,

for their discovery of fullerenes.

Note: This document is made for Netscape 2.0 or later, and some of the chemical formulas might not appear as intended using other browsers.

The discovery of carbon atoms bound in the form of a ball is rewarded

New forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells was discovered in 1985 by **Robert F. Curl, Harold W. Kroto** and **Richard E. Smalley**. The number of carbon atoms in the shell can vary, and for this reason numerous new carbon structures have become known. Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon(VI). The latter two were discovered in 1968 and 1972.

Fullerenes are formed when vaporised carbon condenses in an atmosphere of inert gas. The gaseous carbon is obtained e.g. by directing an intense pulse of laser light at a carbon surface. The released carbon atoms are mixed with a stream of helium gas and combine to form clusters of some few up to hundreds of atoms. The gas is then led into a vacuum chamber where it expands and is cooled to some degrees above absolute zero. The carbon clusters can then be analysed with mass spectrometry.

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms, C_{60}, were the most abundant. They found high stability in C_{60}, which suggested a molecular structure of great symmetry. It was suggested that C_{60} could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodetic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure *buckminsterfullerene* after him.

The discovery of the unique structure of the C_{60} was published in the journal *Nature* and had a mixed reception - both criticism and enthusiastic acceptance. No physicist or chemist had expected that carbon would be found in such a symmetrical form other than those already known. Continuing their work during 1985-90, Curl, Kroto and Smalley obtained further evidence that the proposed structure ought to be correct. Among other things they succeeded in identifying carbon clusters that enclosed one or more metal atoms. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C_{60} by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent. They obtained a mixture of C_{60} and C_{70}, the structures of which could be determined. This confirmed the correctness of the C_{60} hypothesis. The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}. New substances were produced from these compounds, with new and unexpected properties. An entirely new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.

Background

Many widely diverse research areas coincide in the discovery of the fullerenes. **Harold W. Kroto** was at the time active in microwave spectroscopy, a science which thanks to the growth of radioastronomy can be used for analysing gas in space, both in stellar atmospheres and in interstellar gas clouds. Kroto was particularly interested in carbon-rich giant stars. He had discovered and investigated spectrum lines in their atmospheres and found that they could be ascribed to a kind of long-chained molecule of only carbon and nitrogen, termed cyanopolyynes. The same sort of molecules is also found in interstellar gas clouds. Kroto's idea was that these carbon compounds had been formed in stellar atmospheres, not in clouds. He now wished to study the formation of these long-chain molecules more closely.

He got in touch with **Richard E. Smalley**, whose research was in cluster chemistry, an important part of chemical physics. A cluster is an aggregate of atoms or molecules, something in between microscopic particles and macroscopic particles. Smalley had designed and built a special *laser-supersonic cluster beam apparatus* able to vaporise almost any known material into a plasma of atoms and study the design and distribution of the clusters. His paramount interest was clusters of metal atoms, e.g. metals included in semiconductors, and he often performed these investigations together with **Robert F. Curl**, whose background was in microwave and infra-red spectroscopy.

Atoms form clusters

When atoms in a gas phase condense to form clusters, a series is formed where the size of the clusters varies from a few atoms to many hundreds. There are normally two size maxima visible in the distribution curve, one around small clusters and one around large. It is often found that cer-tain cluster sizes may dominate, and the number of atoms in these is termed a "magic number", a term borrowed from nuclear physics. These dominant cluster sizes were assumed to have some special property such as high symmetry.

Fruitful contact

Through his acquaintanceship with Robert Curl, Kroto learned that it should be possible to use Smalley's instrument to study the vaporisation and cluster formation of carbon, which might afford him evidence that the long-carbon-chain compounds could have been formed in the hot parts of stellar atmospheres. Curl conveyed this interest to Smalley and the result was that on 1 September 1985 Kroto arrived in Smalley's laboratory to start, together with Curl and Smalley, the experiments on carbon vaporisation. In the course of the work it proved possible to influence drastically the size distribution of the carbon clusters where, predominantly, 60 appeared as a magic number but also 70 (Fig. 1). The research group

now got something else to think about. Instead of long carbon chains, the idea arose that the C_{60} cluster could have the structure of a truncated (cut off) icosahedron (Fig. 2) since its great stability was assumed to correspond to a closed shell with a highly symmetrical structure. C_{60} was given a fanciful name, buckminsterfullerene, after the American architect R. Buckminster Fuller, inventor of the geodesic dome. This hectic period ended on 12 September with the despatch of a manuscript entitled *C_{60}: Buckminsterfullerene* to *Nature*. The journal received it on 13 September and published the article on 14 November 1985.

Sensational news

For chemists the proposed structure was uniquely beautiful and satisfying. It corresponds to an aromatic, three-dimensional system in which single and double bonds alternated, and was thus of great theoretical significance. Here, moreover, was an entirely new example from a different research tradition with roots in organic chemistry: producing highly symmetrical molecules so as to study their properties. The Platonic bodies have often served as patterns, and hydrocarbons had already been synthesised as tetrahedral, cubic or dodecahedral (12-sided) structures.

Carbon atoms per cluster

Fig. 1
Using mass spectroscopy it was found that the size distribution of carbon clusters could be drastically affected by increasing the degree of chemical "boiling" in the inlet nozzle to the vacuum chamber. Clusters with 60 and 70 carbon atoms could be produced. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Fig. 2
Models of the structures of C_{60}. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Further investigations

To gain further clarity Curl, Kroto and Smalley continued their investigations of C_{60}. They attempted to make it react with other compounds. Gases such as hydrogen, nitrous oxide, carbon monoxide, sulphur dioxide, oxygen or ammonia were injected into the gas stream, but no effect on the C_{60} peak recorded in the mass spectrometer could be demonstrated. This showed that C_{60} was a slow-reacting compound. It also turned out that all carbon clusters with an even number of carbon atoms from 40-80 (the interval that could be studied) reacted equally slowly. Analogously with C_{60} all these should then correspond to entirely closed structures, resembling cages. This was in agreement with Euler's law, a mathematical proposition which states that for any polygon with *n* edges, where *n* is an even number greater than 22, at least one polyhedron can be constructed with 12 pentagons and (*n*-20)/2 hexagons, which, in simple terms, states that it is possible with 12 pentagons and with none or more than one hexagon to construct a polyhedron. For large *n* many different closed structures can occur, thus also for C_{60}, and it was presumably the beautiful symmetry of the proposed structure that gave it the preference.

The combination of chemical inertia in clusters with even numbers of carbon atoms and the possibility that all these could possess closed structures in accordance with Euler's law, led to the proposal that all these carbon clusters should have closed structures. They were given the name fullerenes and conceivably an almost infinite number of fullerenes could exist. The element carbon had thus assumed an almost infinite number of different structures.

C_{60} and metals

New experiments were rapidly devised to test the C_{60} hypothesis. Since the C_{60} structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. A graphite sheet was soaked with a solution of a metal salt (lanthanum chloride, $LaCl_3$) and subjected to vaporisation-condensation experiments. Masspectroscopic analysis of the clusters formed showed the presence of $C_{60}La^+$. These proved to be photoresistant, i.e. irradiation with intense laser light did not remove the metal atoms. This reinforced the idea that metal atoms were captured inside the cage structure.

The possibility of producing clusters with a metal atom enclosed gave rise to what was termed the "shrink-wrapping" experiment. Ions of one and the same size or at least similar sizes were gathered in a magnetic trap and subjected to a laser pulse. It then turned out that the laser beam caused the carbon cage to shrink by 2 carbon atoms at a time: at a certain cage size, when the pressure on the metal atom inside

became too great, the fragmentation ceased. The shell had then shrunk so that it fitted exactly around the metal atom. For $C_{60}Cs^+$ this size was at $C_{48}Cs^+$, for $C_{60}K^+$ it was at $C_{44}K^+$ and for C_{60}^+ at C_{32}^+.

Further strong evidence gave rise to new chemistry

At the end of the 1980s, strong evidence was available that the C_{60} hypothesis was correct. In 1990 the synthesis of macroscopic quantities of C_{60} through carbon arc vaporisation between two graphite electrodes permitted the attainment of full certainty - the whole battery of methods for structure determination could be applied to C_{60} and other fullerenes and completely confirmed the fullerene hypothesis. As opposed to the other forms of carbon the fullerenes represent well-defined chemical compounds with in some respects new properties. A whole new chemistry has developed to manipulate the fullerene structure, and the properties of fullerenes can be studied systematically. It is possible to produce superconducting salts of C_{60}, new three-dimensional polymers, new catalysts, new materials and electrical and optical properties, sensors, and so on. In addition, it has been possible to produce thin tubes with closed ends, nanotubes, arranged in the same way as fullerenes. From a theoretical viewpoint, the discovery of the fullerenes has influenced our conception of such widely separated scientific problems as the galactic carbon cycle and classical aromaticity, a keystone of theoretical chemistry. No practically useful applications have yet been produced, but this is not to be expected as early as six years after macroscopic quantities of fullerenes became available.

Further reading

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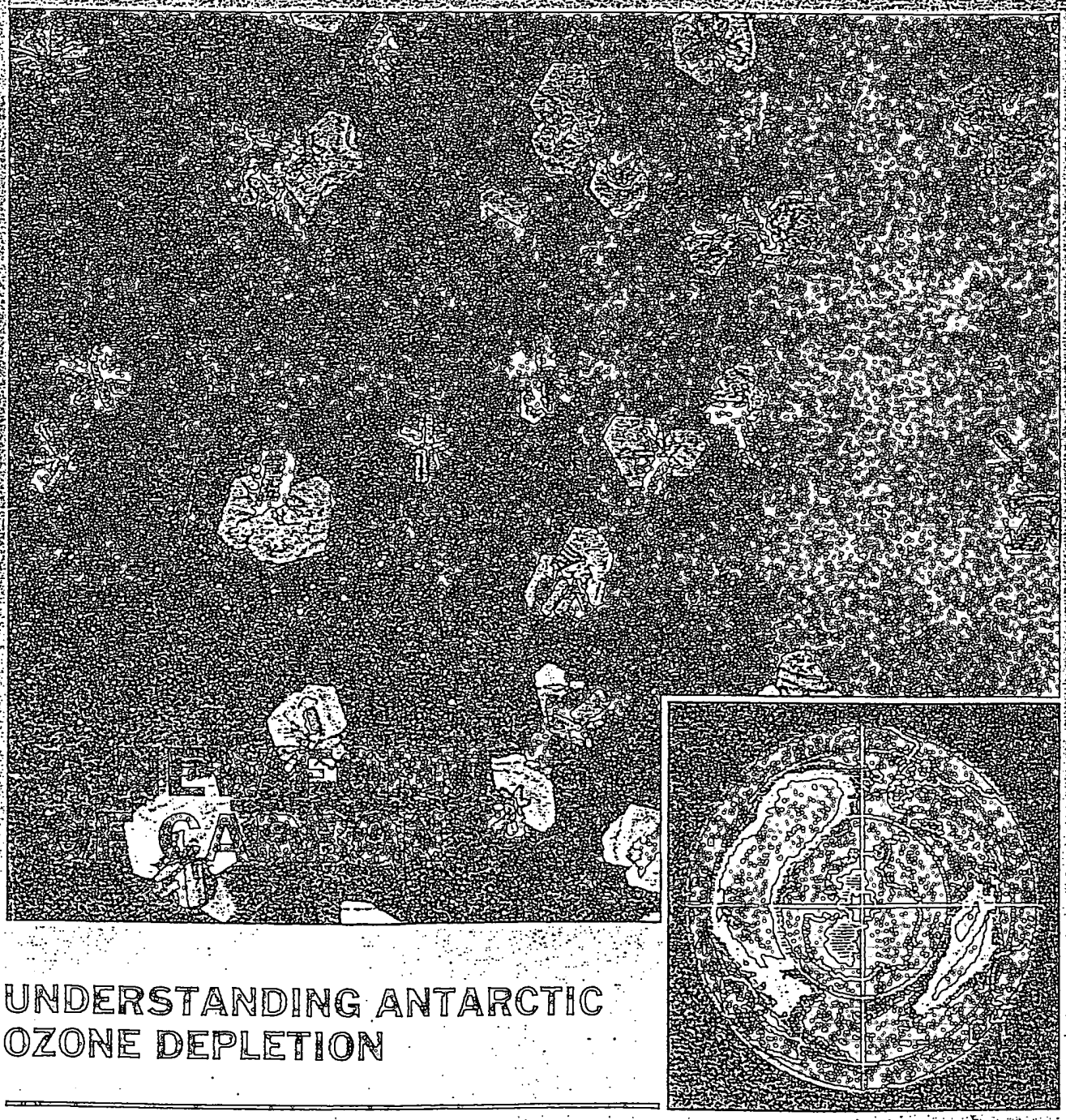

UNDERSTANDING ANTARCTIC OZONE DEPLETION

The cellular defect behind cystic fibrosis

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Solid C_{60}: a new form of carbon

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A new form of pure, solid carbon has been synthesized consisting of a somewhat disordered hexagonal close packing of soccer-ball-shaped C_{60} molecules. Infrared spectra and X-ray diffraction studies of the molecular packing confirm that the molecules have the anticipated 'fullerene' structure. Mass spectroscopy shows that the C_{70} molecule is present at levels of a few per cent. The solid-state and molecular properties of C_{60} and its possible role in interstellar space can now be studied in detail.

FOLLOWING the observation that even-numbered clusters of carbon atoms in the range C_{30}–C_{100} are present in carbon vapour[1], conditions were found[2–4] for which the C_{60} molecule could be made dominant in the large-mass fraction of vapourized graphite. To explain the stability of the molecule, a model was proposed of an elegant structure in which the carbon atoms are arranged at the 60 vertices of a truncated icosahedron, typified by a soccer ball. The structure, dubbed buckminsterfullerene[2] because of its geodesic nature, has been the subject of several theoretical stability tests[5,6] and has been discussed widely in the literature. Calculations of many physical properties have been made, including electron energies[7–9], the optical spectrum[9], vibrational modes[10–15], and the electric and magnetic properties[16,17]. There has been speculation on the possible chemical and industrial uses of C_{60} (ref. 2), and on its importance in astrophysical environments[18–20]. Until now, it has not been possible to produce sufficient quantities of the material to permit measurement of the physical properties, to test the theoretical calculations, or to evaluate the possible applications.

Some of us have recently reported evidence[21,22] for the presence of the C_{60} molecule in soot condensed from evaporated graphite. The identification was based primarily on the observed isotope shifts of the infrared absorptions when ^{12}C was replaced by ^{13}C, and on comparison of the observed features with theoretical predictions. The measured infrared and ultraviolet absorption bands were superimposed on a rather large continuum background absorption from the graphitic carbon which comprised ≥95% of the sample. Here we report how to extract the carrier of the features from the soot, how to purify it, and evidence that the material obtained is in fact primarily C_{60}.

Method of production

The starting material for our process is pure graphitic carbon soot (referred to below as simply soot) with a few per cent by weight of C_{60} molecules, as described in refs 21, 22. It is produced by evaporating graphite electrodes in an atmosphere of ~100 torr of helium. The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene. The material giving rise to the spectral features attributed to C_{60} dissolves to produce a wine-red to brown liquid, depending on the concentration. The liquid is then separated from the soot and dried using gentle heat, leaving a residue of dark brown to black crystalline material. Other non-polar solvents, such as carbon disulphide and carbon tetrachloride, can also dissolve the material. An alternative concentration procedure is to heat the soot to 400 °C in a vacuum or in an inert atmosphere, thus subliming the C_{60} out of the soot (W. Schmidt, personal communication). The sublimed coatings are brown to grey, depending on the thickness. The refractive index in the near-infrared and visible is about two. To purify the material, we recommend removing the ubiquitous hydrocarbons before the concentration procedure is applied (for example, by washing the initial soot with ether). Thin films and powder samples of the new material can be handled without special precautions and seem to be stable in air for at least several weeks, although there does seem to be some deterioration with time for reasons that are as yet unclear. The material can be sublimed repeatedly without decomposition. Using the apparatus described, one person can produce of the order of 100 mg of the purified material in a day.

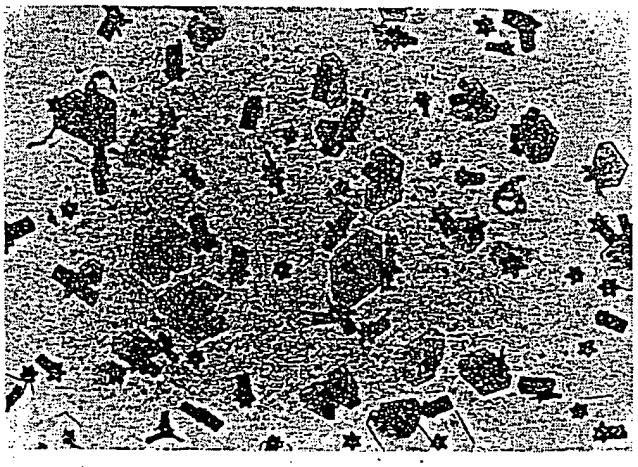

FIG. 1 Transmission micrograph of typical crystals of the C_{60} showing thin platelets, rods and stars of hexagonal symmetry.

Studies by optical microscopy of the material left after evaporating the benzene show a variety of what appear to be crystals—mainly rods, platelets and star-like flakes. Figure 1 shows a micrograph of such an assemblage. All crystals tend to exhibit six-fold symmetry. In transmitted light they appear red to brown in colour; in reflected light the larger crystals have a metallic appearance whereas the platelets show interference colours. The platelets can be rather thin and are thus ideally suited for electron-diffraction studies in an electron microscope (see the inset in Fig. 3).

Mass spectroscopy

The material has been analysed by mass spectrometry at several facilities. All mass spectra have a strong peak at mass 720 a.m.u., the mass of C_{60}. Significant differences in the spectra occur only at masses lower than 300 a.m.u. Most of these differences seem to originate from the different ionization techniques and in the different methods of desorbing molecules from the sample. Mass spectra recorded at low and high resolution are shown in Fig. 2. The spectra were obtained using a time-of-flight secondary-ion mass spectrometer[23] and a C_{60}-coated stainless-steel plate. In the mass range above 300 a.m.u., the spectrum is dominated by C_{60} ions and its fragments (even-numbered clusters of atomic carbon), and C_{70} ions. In this sample, the ratio of C_{70} to C_{60} is

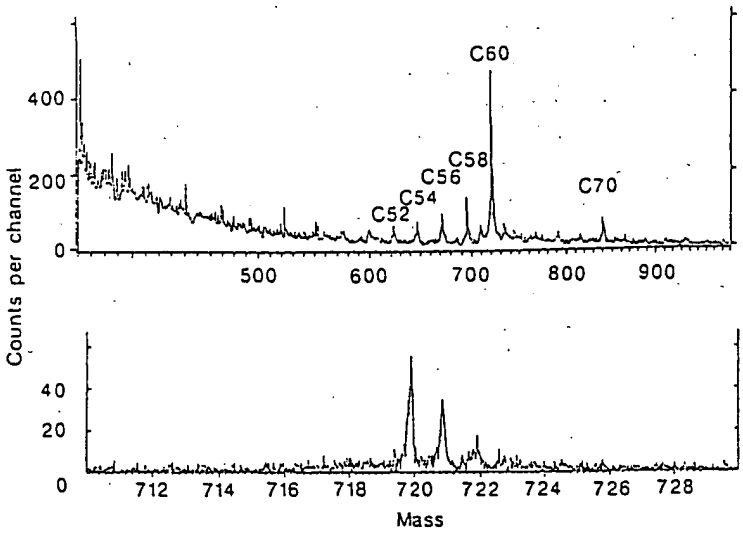

FIG. 2 Low-resolution (top) and high-resolution time-of-flight mass spectra of positive ions obtained from coatings of solid C_{60}. A 5-keV Ar^+ ion beam was used to sputter and ionize the sample. The isotope pattern (bottom) is approximately that expected for C_{60} molecules composed of ^{12}C and ^{13}C isotopes of natural abundance.

~0.1. The high-resolution mass spectrum shows approximately the expected isotope pattern for C_{60}. The increasing background in the low-resolution mass spectrum is not produced by the sample—such backgrounds also occur in blank measurements on uncoated stainless-steel substrates.

So far, the cleanest mass spectra have been obtained when the material was evaporated and ionized in the vapour phase by electrons. In such spectra the low-mass background is substantially reduced and the entire mass spectrum is dominated by C_{60} ions and its fragments. The ratio of C_{70} to C_{60} in these mass spectra is ~0.02 and seems to be smaller than that shown in Fig. 2. Both ratios are of the order of those reported from laser-evaporation experiments[2,3]. We assume, as previously suggested[24], that the C_{70} molecule also has a closed-cage structure, either elongated[24] or nearly spherical[25]. Further details of the mass spectroscopy of the new material will be published elsewhere.

Structure

To determine if the C_{60} molecules form a regular lattice, we performed electron and X-ray diffraction studies on the individual crystals and on the powder. A typical X-ray diffraction pattern of the C_{60} powder is shown in Fig. 3. To aid in comparing the electron diffraction results with the X-ray results we have inset the electron diffraction pattern in Fig. 3. From the hexagonal array of diffraction spots indexed as shown in the figure, a d spacing of 8.7 Å was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The most obvious correspondence between the two types of diffraction is between the peak at 5.01 Å of the X-ray pattern and the (110) spot of the electron diffraction pattern, which gives a spacing of ~5.0 Å. Assuming that the C_{60} molecules are behaving approximately as spheres stacked in a hexagonal close-packed lattice with a c/a ratio of 1.633, d spacings can be calculated. The results are shown in Table 1. The values derived from this interpretation are $a = 10.02$ Å and $c = 16.36$ Å. The nearest-neighbour distance is thus 10.02 Å. For such a crystal structure the density is calculated to be 1.678 g cm^{-3}, which is consistent with the value of 1.65 ± 0.05 g cm^{-3} determined by suspending crystal samples in aqueous $GaCl_3$ solutions of known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions suggest that the order is less than perfect. Further, X-ray diffraction patterns from carefully grown crystals up to 500 μm in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micrometre-sized crystals). It therefore appears that these larger crystals do not exhibit long-range periodicity in all directions.

A likely explanation for these facts lies in the disordered stacking of the molecules in planes normal to the c axis. It is well known that the positions taken by spheres in the third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in a face-centred cubic structure being ABCABC... whereas that in a hexagonal close-

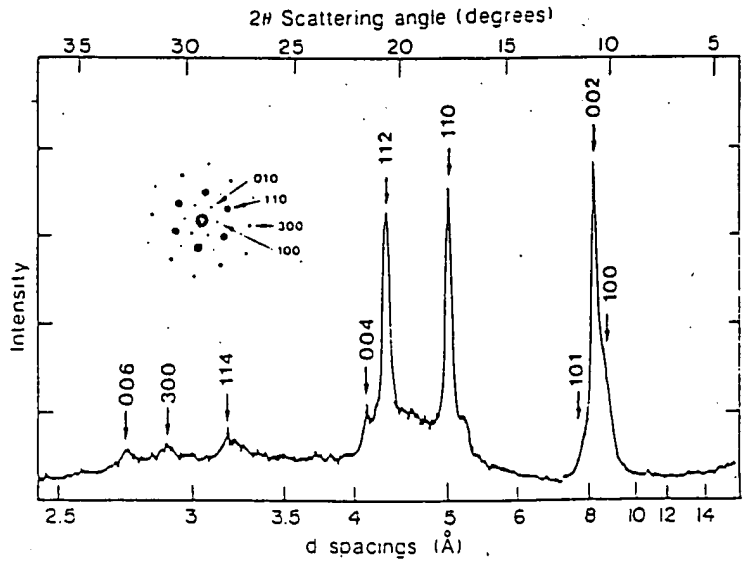

FIG. 3 X-ray diffraction pattern of a microcrystalline powder of C_{60}. Inset (upper left) is a single-crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern. The pattern is from a thin platelet such as those in Fig. 1 with the electron beam perpendicular to the flat face.

TABLE 1 X-ray diffraction results

Measured 2θ (deg)	Measured d spacing (Å)	Calculated d spacing (Å)	Assignment (hkl)
10.2 shoulder	8.7	8.68	(100)
10.81	8.18	8.18	(002)
		7.68	(101)
17.69	5.01	5.01	(110)
20.73	4.28	4.28	(112)
21.63	4.11	4.09	(004)
28.1	3.18	3.17	(114)
30.8	2.90	2.90	(300)
32.7	2.74	2.73	(006)

* Assignments for a hexagonal lattice using $a=10.02$ Å, $c=16.36$ Å. $(1/d^2)=\frac{4}{3}[(h^2+hk+k^2)/a^2]+l^2/c^2$.

packed structure is ABABAB ... If the stacking sequence varies, the X-ray lines owing to certain planes will be broadened by the disorder whereas other lines will remain sharp. Such disordered crystalline behaviour was observed long ago in the hexagonal close-packed structure of cobalt[26-28] where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened by the stacking disorder. Reflections from planes such as (002) remain sharp because these planes have identical spacings in the face-centred cubic and hexagonal close-packed structures. For the planes producing broadened diffraction peaks because of this kind of disorder, the following condition for the Miller indices (hkl) has been shown to apply[27,29]: $h-k=3t\pm1$ (where t is an integer) and $l\neq0$. None of these broadened reflections are apparent in the X-ray pattern of Fig. 3. This may explain the weakness of the characteristically strong (101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated C_{70} molecule has yet to be determined.

In small crystals at least, the C_{60} molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, which is entirely consistent with the hypothesis that they are shaped like soccer balls. The excess between the nearest-neighbour distance (10.02 Å) and the diameter calculated for the carbon cage itself (7.1 Å) must represent the effective van der Waals diameter set by the repulsion of the π electron clouds extending outward from each carbon atom. Because the van der Waals diameter of carbon is usually considered to be 3.3–3.4 Å the packing seems a little tighter than one might expect for soccer-ball-shaped C_{60} molecules. The reason for this has not yet been determined.

In summary, our diffraction data imply that the substance isolated is at least partially crystalline. The inferred lattice constants, when interpreted in terms of close-packed icosahedral C_{60}, yield a density consistent with the measured value. Further evidence that the molecules are indeed buckminsterfullerene and that the solid primarily consists of these molecules comes from the spectroscopic results.

Spectroscopy

The absorption spectra of the graphitic soot[21,22] showed evidence for the presence of C_{60} in macroscopic quantities. Following the purification steps described above the material can be studied spectroscopically with the assurance that the spectra are dominated by C_{60}, with some possible effects from C_{70}. Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimation chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of C_{60} smoke (sub-micrometre microcrystalline particles of solid C_{60}) with the particle size depending to some extent on the pressure.

Figure 4 shows the transmission spectrum of an ~2-μm-thick C_{60} coating on a silicon substrate. The infrared bands are at the same positions as previously reported[21,22], with the four most

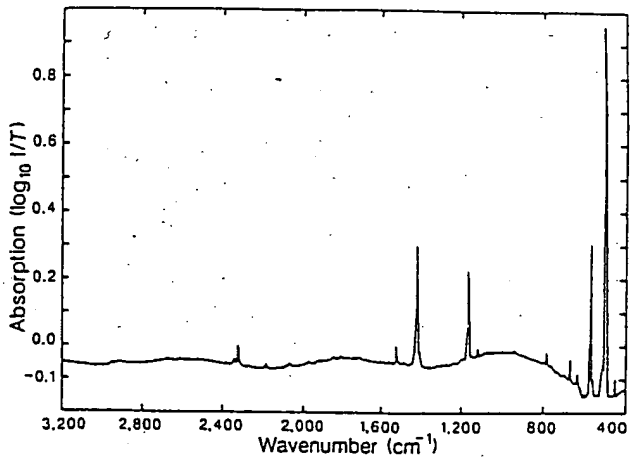

FIG. 4 Infrared absorption spectrum of a coating, ~2 μm thick, of solid C_{60} on a silicon substrate, referenced to a clean silicon substrate. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

intense lines at 1,429, 1,183, 577 and 528 cm^{-1}; here, however, there is no underlying continuum remaining from the soot. In many of our early attempts to obtain pure C_{60}, there was a strong band in the vicinity of 3.0 μm, which is characteristic of a CH-stretching mode. After much effort this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Fig. 4 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities. Vibrational modes to compare with the measured positions of the four strong bands have been calculated by several workers[10-15]. As noted previously, the presence of only four strong bands is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the C_{70} molecule or symmetry-breaking produced (for example) by isotopes other than ^{12}C in the C_{60} molecule or by mutual interaction of the C_{60} molecules in the solid. Weaker features at ~2,330 and 2,190 cm^{-1}, located in the vicinity of the free CO_2 and CO stretching modes, may imply some attachment of the CO_2 or CO to a small fraction of the total number of C_{60} molecules. Another notable feature is the peak at 675 cm^{-1}, which is weak in the thin-film substrates but almost as strong as the four main features in the crystals. We suspect that this vibrational mode may be of solid state rather than molecular origin.

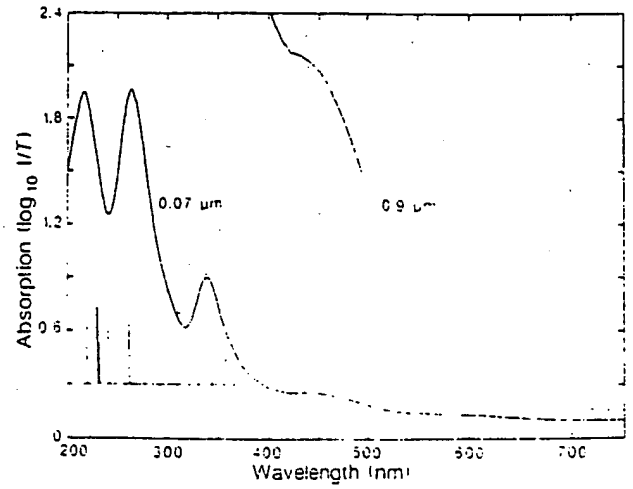

FIG. 5 Visible-ultraviolet absorption spectra of two thicknesses of solid C_{60} on quartz. The calculated[9] positions and relative oscillator strengths for allowed transitions of C_{60} are shown on the bottom.

Figure 5 shows an absorption spectrum taken on a uniform film coated on a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra[22]. Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a plateau between ~460 and 500 nm and a small peak near 625 nm. At the bottom of Fig. 5 we have shown positions and relative oscillator strengths taken from Larsson, Volosov and Rosén[9] calculated for the C_{60} molecule. They also reported a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between our measurements on solid films and the allowed transitions predicted for the molecule. The possibility exists, however, that one or more of the absorption features shown in Fig. 5 are due to C_{70}. We still do not observe a band at 386 nm in our films, as observed[30] using a laser depletion spectroscopy method and attributed to the C_{60} molecule. Quite similar spectra to that in Fig. 5 have been recorded for microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268 and 345 nm.

Possible interstellar dust

The original stimulus for the work[2] that led to the hypothesis of the soccer-ball-shaped C_{60} molecule, buckminsterfullerene, was an interest in certain unexplained features in the absorption and emission spectra of interstellar matter. These include an intense absorption band at 217 nm which has long been attributed to small particles of graphite[31], a group of unidentified interstellar absorption bands in the visible that have defied explanation for more than 70 years[31,32], and several strong emission bands attributed to polycyclic aromatic hydrocarbons[33,34]. Based on the visible and infrared absorption spectra of Figs 4 and 5, we do not see any obvious matches with the interstellar features. The ultraviolet band at 216–219 nm has a similar peak wavelength to an interstellar feature, although the other strong bands of the spectrum have no interstellar counterparts. As the influence of C_{70} absorptions on the spectrum is not yet known, a conclusive comparison with the 217-nm interstellar band is difficult. We note that the visible-ultraviolet spectrum presented here is characteristic of a solid, rather than of free molecules. In addition, these new results do not relate directly to absorption in the free C_{60}^{+} molecular ion, which has been envisaged[19] to explain the diffuse interstellar bands. Nevertheless, these data should now provide guidance for possible infrared detection of the C_{60} molecule, if it is indeed as ubiquitous in the cosmos as some have supposed.

Summary

To our method for producing macroscopic quantities of C_{60}, we have added a method for concentrating it in pure solid form. Analyses including mass spectroscopy, infrared spectroscopy, electron diffraction and X-ray diffraction leave little doubt that we have produced a solid material that apparently has not been reported previously. We call the solid fullerite as a simple extension of the shortened term fullerene, which has been applied to the large cage-shaped molecules typified by buckminsterfullerene (C_{60}). The various physical and chemical properties of C_{60} can now be measured and speculations concerning its potential uses can be tested. □

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ACKNOWLEDGEMENTS. W.K. and K.F. thank our colleagues F. Arnold, J. Kissel, O. Möhler, G. Natour, P. Sölter, H. Zscheeg, H. H. Eysel, B. Nuber, W. Kühlbrandt, M. Rentzea and J. Sawatzki. L.D.L. and D.R.H. thank our colleagues J. T. Emmert, D. L. Bentley, W. Bilodeau, K. H. Schramm and D. R. Luffer. D.R.H. thanks the Alexander von Humboldt Stiftung for a senior US Scientist award. We also thank H. W. Kroto and R. F. Curl for discussions.

EXHIBIT C1

53. A solid carbon product prepared by the process comprising:

(a) vaporizing a carbon source in the presence of an inert quenching gas under conditions effective to provide a sooty carbon product comprising C_{60} molecules;

(b) depositing the sooty carbon product on a collecting substrate;

(c) removing the sooty carbon product form the collecting substrate;

(d) contacting the sooty carbon product with a non-polar organic solvent effective to dissolve C_{60} molecules, said solvent being present in an amount effective to dissolve the C_{60} molecules in said sooty carbon product; and

(e) recovering from said resulting product formed when the sooty carbon product was contacted with said solvent a solid carbon product comprising C_{60} in a macroscopic amount.

54. The solid carbon product of Claim 53 in which the carbon in step (a) is vaporized in an evacuated reactor.

55. The solid carbon product of Claim 54 in which the carbon source of step (a) is vaporized in an evacuated bell jar.

56. The solid carbon product of Claim 53 in which the carbon source subject to vaporization in step (a) is graphite.

57. The solid carbon product of Claim 53 in which the carbon source subject to vaporization in step (a) is graphite rods.

58. The solid carbon product of Claim 53 wherein the carbon source is vaporized in step (a) through heating the carbon source by means of an electrical current of sufficient intensity to produce the sooty carbon product.

59. The solid carbon product of Claim 58 wherein the electrical current is about 100 amps.

60. The solid carbon product of Claim 53 wherein the inert quenching gas of step (a) is a noble gas.

61. The solid carbon product of Claim 53 wherein the carbon source is vaporized in step (a) at a pressure ranging from 50 torr to 400 torr.

62. The solid carbon product of Claim 61 wherein the carbon is vaporized in step (a) at approximately 100 torr.

63. The solid carbon product of Claim 53 wherein the carbon is vaporized in step (a) at a pressure ranging from about 2 to 3 atmospheres.

64. The solid carbon product of Claim 53 wherein the collecting substrate in step (b) is a glass surface.

65. The solid carbon product of Claim 60 wherein the inert gas is helium or argon.

66. The solid carbon product of Claim 53 wherein the non-polar organic solvent of step (d) is carbon dissulfide, benzene, carbon tetrachloride or toluene.

67. The solid carbon product of Claim 66 wherein the solvent is benzene.

68. The solid carbon product of Claim 66 wherein the solvent is carbon tetrachloride.

69. The solid carbon product of Claim 53 wherein recovery step (e) comprises evaporating the solvent.

70. The solid carbon product of Claim 53 further comprising C_{70}.

71. The solid carbon product of Claim 53 further comprising:

(f) purifying the carbon product of step (e) to obtain C_{60}.

72. The solid product of Claim 71 wherein the purification of step (f) is sublimation at 300-400°C, fractional crystallization, column chromatography, capillary electrophoresis, HPLC, preparative thin layer chromatography, crystallization or extraction.

73. A formed or molded product comprising crystalline C_{60}.

75. A free flowing particulate comprised of crystalline C_{60}.

80. A formed or molded product comprising solid C_{70}.

81. A free-flowing particulate comprising solid C_{70}.

84. Substantially pure C_{60}.

85. Substantially pure solid C_{60}.

86. C_{60} in a macroscopic amount.

89. Substantially pure C_{70}.

90. Substantially pure solid C_{70}.

92. Crystalline C_{60}.

93. Crystalline C_{70}.

94. Substantially pure crystalline C_{60}.

95. Substantially pure crystalline C_{70}.

96. C_{70} in a macroscopic amount.

102. A macroscopic amount of substantially pure C_{60}.

103. A macroscopic amount of substantially pure C_{70}.

104. A formed or molded product comprising C_{70}, said C_{70} being present in a macroscopic amount.

105. A free flowing particulate comprising C_{70}, said C_{70} being present in a macroscopic amount.

106. A formed or molded product comprising C_{60}, said C_{60} being present in a macroscopic amount.

107. A free flowing particulate comprising C_{60}, said C_{60} being present in a macroscopic amount.

111. A solid comprising C_{60}, said C_{60} being present in a macroscopic amount.

112. A solid comprising C_{70}, said C_{70} being present in a macroscopic amount.

113. A sooty product comprising C_{60}, the C_{60} in said sooty product being present in sufficient concentration to allow a macroscopic amount of said C_{60} to be separated therefrom.

114. A sooty product comprising C_{70}, the C_{70} in said sooty product being present in sufficient concentration to allow a macroscopic amount of said C_{70} to be separated therefrom.

119. A sooty carbon product prepared by the process comprising:

(a) vaporizing a carbon source in the presence of an inert gas to provide a vapor of carbon atoms,

(b) quenching said vapor of carbon in said inert gas under conditions effective to nucleate and condense said vapor of carbon atoms into a sooty carbon product comprising C_{60} molecules, said C_{60} molecules being present in said sooty carbon in sufficient concentrations to allow a macroscopic amount of C_{60} to be separated from said soot.

122. The sooty carbon product of Claim 113, additionally comprising C_{70}.

123. The sooty carbon product of Claim 119 additionally comprising C_{70}.

124. The sooty carbon product of Claim 119 in which the carbon source subject to vaporization in step (a) is graphite or amorphous or glassy carbon.

125. The sooty carbon product of Claim 119 in which the carbon source subject to vaporization in step (a) is graphite.

126. The sooty carbon product of Claim 119 in which the carbon source subject to vaporization in step (a) is graphite rods.

127. The sooty carbon product of Claim 119 in which the carbon source in step (a) is vaporized in an evacuated reactor.

128. The sooty carbon product of Claim 119 in which the carbon source in step (a) is vaporized in an evacuated bell jar.

129. The sooty carbon product of Claim 119 in which the inert gas is a noble gas.

130. The sooty carbon product of Claim 129 in which the noble gas is helium or argon.

131. The sooty carbon product of Claim 119 in which the process is conducted at a pressure sufficient to nucleate said carbon vapor.

132. The sooty carbon product of Claim 131 in which the pressure ranges from 60 torr to 400 torr.

141. A solid carbon product prepared by the process comprising:

(a) evaporating a carbon source in the presence of an inert quenching gas under conditions effective to produce a sooty carbon product containing C_{60}, said C_{60} being present in said sooty carbon product in sufficient concentration to allow a macroscopic amount of said C_{60} to be separated from said sooty product;

(b) collecting the sooty carbon product produced therefrom;

(c) subliming the carbon product comprising C_{60} from the sooty carbon product; and

(d) condensing the sublimed carbon product comprising C_{60}.

142. The solid carbon product of Claim 141 wherein the sublimation occurs at a temperature ranging from 300°-400°C.

143. The solid carbon product of Claim 142 wherein step (c) comprises heating the carbon product comprising C_{60} in a vacuum or inert atmosphere at effective sublimation temperatures to extract the carbon product comprising C_{60} from said sooty carbon product.

144. The solid carbon product of Claim 141 in which the carbon source in step (a) is vaporized in an evacuated reactor.

145. The solid carbon product of Claim 144 in which the carbon in step (a) is vaporized in an evacuated bell jar.

146. The solid carbon product of Claim 141 in which the carbon subject to vaporization in step (a) is graphite.

147. The solid carbon product of Claim 141 in which the carbon subject to vaporization in step (a) is graphite rods.

148. The solid carbon product of Claim 141, wherein the carbon source in step (a) is vaporized by passing an electric current of sufficient intensity to produce a sooty carbon product.

149. The solid carbon product of Claim 148, wherein the electrical current is about 100 amps.

150. The solid carbon product of Claim 141, wherein the inert quenching gas of step (a) is a noble gas.

151. The solid carbon product of Claim 141, wherein the carbon source in step (a) is vaporized at a pressure ranging from 50 torr to 400 torr.

152. The solid carbon product of Claim 151, wherein the carbon source is vaporized in step (a) at approximately 100 torr.

153. The solid carbon product of Claim 53, wherein the collecting substrate in step (b) is a glass surface.

154. The solid carbon product of Claim 150, wherein the noble gas is helium or argon.

155. The solid carbon product of Claim 141, wherein C_{70} is additionally present.

156. The solid carbon product of Claim 155 wherein C_{70} is separated from C_{60} by sublimination, column chromatography, fractional crystallization, capillary electrophoresis, HPLC, preparative thin layer chromatography, or extraction.

157. The solid carbon product of Claim 155, wherein the C_{70} is separated from C_{60} by sublimation.

162. The solid carbon product according to Claim 155, wherein the C_{70} is present in a macroscopic amount.

165. A solid comprising a macroscopic amount of crystalline C_{60}.

166. A solid comprising a macroscopic amount of crystalline C_{70}.

167. A carbon product comprising a macroscopic amount of solid C_{60}.

168. A carbon product comprising a macroscopic amount of solid C_{70}.

169. The carbon product of Claim 167, wherein the solid C_{60} is crystalline C_{60}.

170. The carbon product of Claim 168, wherein the solid C_{70} is crystalline C_{70}

EXHIBIT C2

53. A solid carbon product prepared by the process comprising:

(a) vaporizing a carbon source in the presence of an inert quenching gas under conditions effective to provide a sooty carbon product comprising C_{60} molecules;

(b) depositing the sooty carbon product on a collecting substrate;

(c) removing the sooty carbon product form the collecting substrate;

(d) contacting the sooty carbon product with a non-polar organic solvent effective to dissolve C_{60} molecules, said solvent being present in an amount effective to dissolve the C_{60} molecules in said sooty carbon product; and

(e) recovering from said resulting product formed when the sooty carbon product was contacted with said solvent a solid carbon product comprising C_{60} in a macroscopic amount.

54. The solid carbon product of Claim 53 in which the carbon in step (a) is vaporized in an evacuated reactor.

55. The solid carbon product of Claim 54 in which the carbon source of step (a) is vaporized in an evacuated bell jar.

56. The solid carbon product of Claim 53 in which the carbon source subject to vaporization in step (a) is graphite.

57. The solid carbon product of Claim 53 in which the carbon source subject to vaporization in step (a) is graphite rods.

58. The solid carbon product of Claim 53 wherein the carbon source is vaporized in step (a) through heating the carbon source by means of an electrical current of sufficient intensity to produce the sooty carbon product.

59. The solid carbon product of Claim 58 wherein the electrical current is about 100 amps.

60. The solid carbon product of Claim 53 wherein the inert quenching gas of step (a) is a noble gas.

61. The solid carbon product of Claim 53 wherein the carbon source is vaporized in step (a) at a pressure ranging from 50 torr to 400 torr.

62. The solid carbon product of Claim 61 wherein the carbon is vaporized in step (a) at approximately 100 torr.

63. The solid carbon product of Claim 53 wherein the carbon is vaporized in step (a) at a pressure ranging from about 2 to 3 atmospheres.

64. The solid carbon product of Claim 53 wherein the collecting substrate in step (b) is a glass surface.

65. The solid carbon product of Claim 60 wherein the inert gas is helium or argon.

66. The solid carbon product of Claim 53 wherein the non-polar organic solvent of step (d) is carbon dissulfide, benzene, carbon tetrachloride or toluene.

67. The solid carbon product of Claim 66 wherein the solvent is benzene.

68. The solid carbon product of Claim 66 wherein the solvent is carbon tetrachloride.

69. The solid carbon product of Claim 53 wherein recovery step (e) comprises evaporating the solvent.

70. The solid carbon product of Claim 53 further comprising C_{70}.

71. The solid carbon product of Claim 53 further comprising:

(f) purifying the carbon product of step (e) to obtain C_{60}.

72. The solid product of Claim 71 wherein the purification of step (f) is sublimation at 300-400°C, column chromatography, capillary electrophoresis, preparative thin layer chromatography, crystallization or extraction.

73. A formed or molded product comprising crystalline C_{60}.

75. A free flowing particulate comprised of crystalline C_{60}.

80. A formed or molded product comprising solid C_{70}.

81. A free-flowing particulate comprising solid C_{70}.

84. Substantially pure C_{60}.

85. Substantially pure solid C_{60}.

86. C_{60} in a macroscopic amount.

89. Substantially pure C_{70}.

90. Substantially pure solid C_{70}.

92. Crystalline C_{60}.

93. Crystalline C_{70}.

94. Substantially pure crystalline C_{60}.

95. Substantially pure crystalline C_{70}.

96. C_{70} in a macroscopic amount.

102. A macroscopic amount of substantially pure C_{60}.

103. A macroscopic amount of substantially pure C_{70}.

104. A formed or molded product comprising C_{70}, said C_{70} being present in a macroscopic amount.

105. A free flowing particulate comprising C_{70}, said C_{70} being present in a macroscopic amount.

106. A formed or molded product comprising C_{60}, said C_{60} being present in a macroscopic amount.

107. A free flowing particulate comprising C_{60}, said C_{60} being present in a macroscopic amount.

111. A solid comprising C_{60}, said C_{60} being present in a macroscopic amount.

112. A solid comprising C_{70}, said C_{70} being present in a macroscopic amount.

113. A sooty product comprising C_{60}, the C_{60} in said sooty product being present in sufficient concentration to allow a macroscopic amount of said C_{60} to be separated therefrom.

114. A sooty product comprising C_{70}, the C_{70} in said sooty product being present in sufficient concentration to allow a macroscopic amount of said C_{70} to be separated therefrom.

119. A sooty carbon product prepared by the process comprising:

(a) vaporizing a carbon source in the presence of an inert gas to provide a vapor of carbon atoms,

(b) quenching said vapor of carbon in said inert gas under conditions effective to nucleate and condense said vapor of carbon atoms into a sooty carbon product comprising C_{60} molecules, said C_{60} molecules being present in said sooty carbon in sufficient concentrations to allow a macroscopic amount of C_{60} to be separated from said soot.

122. The sooty carbon product of Claim 113, additionally comprising C_{70}.

123. The sooty carbon product of Claim 119 additionally comprising C_{70}.

124. The sooty carbon product of Claim 119 in which the carbon source subject to vaporization in step (a) is graphite or amorphous or glassy carbon.

125. The sooty carbon product of Claim 119 in which the carbon source subject to vaporization in step (a) is graphite.

126. The sooty carbon product of Claim 119 in which the carbon source subject to vaporization in step (a) is graphite rods.

127. The sooty carbon product of Claim 119 in which the carbon source in step (a) is vaporized in an evacuated reactor.

128. The sooty carbon product of Claim 119 in which the carbon source in step (a) is vaporized in an evacuated bell jar.

129. The sooty carbon product of Claim 119 in which the inert gas is a noble gas.

130. The sooty carbon product of Claim 129 in which the noble gas is helium or argon.

131. The sooty carbon product of Claim 119 in which the process is conducted at a pressure sufficient to nucleate said carbon vapor.

132. The sooty carbon product of Claim 131 in which the pressure ranges from 60 torr to 400 torr.

141. A solid carbon product prepared by the process comprising:

(a) evaporating a carbon source in the presence of an inert quenching gas under conditions effective to produce a sooty carbon product containing C_{60}, said C_{60} being present in said sooty carbon product in sufficient concentration to allow a macroscopic amount of said C_{60} to be separated from said sooty product;

(b) collecting the sooty carbon product produced therefrom;

(c) subliming the carbon product comprising C_{60} from the sooty carbon product; and

(d) condensing the sublimed carbon product comprising C_{60}.

142. The solid carbon product of Claim 141 wherein the sublimation occurs at a temperature ranging from 300°-400°C.

143. The solid carbon product of Claim 142 wherein step (c) comprises heating the carbon product comprising C_{60} in a vacuum or inert atmosphere at effective sublimation temperatures to extract the carbon product comprising C_{60} from said sooty carbon product.

144. The solid carbon product of Claim 141 in which the carbon source in step (a) is vaporized in an evacuated reactor.

145. The solid carbon product of Claim 144 in which the carbon in step (a) is vaporized in an evacuated bell jar.

146. The solid carbon product of Claim 141 in which the carbon subject to vaporization in step (a) is graphite.

147. The solid carbon product of Claim 141 in which the carbon subject to vaporization in step (a) is graphite rods.

148. The solid carbon product of Claim 141, wherein the carbon source in step (a) is vaporized by passing an electric current of sufficient intensity to produce a sooty carbon product.

149. The solid carbon product of Claim 148, wherein the electrical current is about 100 amps.

150. The solid carbon product of Claim 141, wherein the inert quenching gas of step (a) is a noble gas.

151. The solid carbon product of Claim 141, wherein the carbon source in step (a) is vaporized at a pressure ranging from 50 torr to 400 torr.

152. The solid carbon product of Claim 151, wherein the carbon source is vaporized in step (a) at approximately 100 torr.

153. The solid carbon product of Claim 53, wherein the collecting substrate in step (b) is a glass surface.

154. The solid carbon product of Claim 150, wherein the noble gas is helium or argon.

155. The solid carbon product of Claim 141, wherein C_{70} is additionally present.

156. The solid carbon product of Claim 155, wherein C_{70} is separated from C_{60} by sublimation, column chromatography, fractional crystallization, capillary electrophoresis, preparative thin layer chromatography, or extraction.

157. The solid carbon product of Claim 155, wherein the C_{70} is separated from C_{60} by sublimation.

158.-161. (Cancelled)

162. The solid carbon product according to Claim 155, wherein the C_{70} is present in a macroscopic amount.

165. A solid comprising a macroscopic amount of crystalline C_{60}.

166. A solid comprising a macroscopic amount of crystalline C_{70}.

167. A carbon product comprising a macroscopic amount of solid C_{60}.

168. A carbon product comprising a macroscopic amount of solid C_{70}.

169. The carbon product of Claim 167, wherein the solid C_{60} is crystalline C_{60}.

170. The carbon product of Claim 168, wherein the solid C_{70} is crystalline C_{70}.

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman Examiner:

Serial No.: 08/236,933 Art Unit:

Filed: May 2, 1994 Docket: 7913ZAZY

For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231

DECLARATION OF Harold W. Kroto UNDER 37 C.F.R. §1.132

Sir:

I, Harold W. Kroto, Ph. D., declare and say as follows:

1. I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom. I have attached for the convenience of the United States Patent Office a copy of my curriculum vitae as Exhibit 1, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2. I have reviewed the above-identified application, the Preliminary Amendment therein and the following reference documents, which I understand to be cited in support of a rejection of the present application.

1. an article by K.S. Day, et al., Nature Physical Science 1973, 243, 50-51.

2. an article by Iijima, et al., in J.Phys. Chem. 1987, 91, 3466-3467. ("Iijima et al".).

3. Translation of Russian Patent No. 1,587,000.

4. U.S. Patent No. 2,957,756 to R. Bacon.

5. an article by Kappler, et al., in J. App. Phys., 1979, 50, 308-316.

3. The application teaches in clear detail to the skilled artisan the preparation of fullerenes, including C_{60}, in quantities that were never recognizably achieved before the discovery by Huffman and Kratschmer described in the application. Specifically, the application describes methods for the production of C_{60} and C_{70} in macroscopic amounts, i.e., amounts that could be seen with the naked eye (inherently at least 10^{18} molecules of product). That discovery for the first time permitted the researchers to confirm the existence and structure of these materials, including subjecting them to general testing of their detailed properties and characteristics, which had theretofore only been projected based upon educated speculation and calculation, grounded upon circumstantial evidence of their existence.

4. I am intimately familiar with the literature concerning and was personally involved in the search for C_{60} and the greater fullerene family: for convenience, one may refer particularly to our review of the literature through 1990 described in an article entitled "C_{60} Buckminsterfullerene, in Chem. Rev. 1991, 1231-1235 attached hereto as Exhibit 2 and for my personal involvement in the research effort in my article entitled " C_{60}: Buckminster-fullerene, the Celestial Sphere that Fell to Earth" in Angewandte Chemie I.E.E. 1992, 31, 111-129, attached as Exhibit 3.

5. I believe it is fair to say that I am among the recognized experts in the subject of fullerenes, and that I was quite cognizant of the state of the art in 1990, and of the early attempted preparation and identification of fullerenes, especially C_{60} and C_{70}.

6. I am familiar with the work of Huffman and Kratschmer on this subject having closely followed their research as described in the Angewandte Chemie article referred to above and attached as Exhibit 3.

7. I am also familiar with the methods described in the above-identified patent application of Huffman and Kratschmer and utilize their principles regularly in producing quantities of C_{60} for research purposes in our laboratories,

8. In my professional opinion the methods for producing the fullerenes, including C_{60}, are described in the application in such manner as to enable one skilled in the art to make and use the same.

9. In my professional opinion, the reference documents listed in paragraph 2 hereinabove, taken individually or collectively, do not teach nor do they claim to teach methods for the production of fullerenes, including C_{60}; nor is there provided evidence of the production of any such product. Specifically, it cannot be stated that there is any reliable scientific evidence of the formation of C_{60} or C_{70} in any of the references, and no assertion is made that quantities of C_{60} or C_{70} were made. In fact, any such assertion would be entirely speculative and unsupported; to my knowledge, no researcher had proven possession of C_{60} or C_{70} prior to Huffman and Kratschmer.

While Iijima et al alleges that they saw a molecule of C_{60} in the middle of a carbon particle this conclusion is similarly entirely speculative and unsupported by the evidence. Furthermore, Iijima et al did not report in that article a methodolgy capable of producing and isolating fullerenes in

10. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of C_{60} and C_{70} by the methods described in the above-identified application is recognized by the knowledgeable scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as C_{60} could be achieved by these methods, as it was expected that no more than < 1/10000 parts of target molecules would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

11. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite remarkable. This is readily appreciated if one considers the historical perspective. Ever since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 5, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each were unsuccessful. Finally, to my knowledge, one group, Huffman and Kratschmer, were the first to find a methodology capable of producing and isolating fullerenes, such as C_{60}, in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

12. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical predictions about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating more than four thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes.

13. I have been requested as well to examine the claims presented by applicants Huffman and Kratschmer. I am not qualified in the law as to the interpretation of claims; but as a scientist knowledgeable in this art, I find the qualifying terms to be aptly descriptive of the methods described and the products produced in the above-identified application, consistently with scientific usage at the time the application was filed.

14. I further assert that the term "macroscopic" aptly and correctly characterizes the breakthrough made by Huffman and Kratschmer in permitting isolation and characterization of the fullerenes C_{60} and C_{70}, in that the term expressly denotes that which can be seen (and therefore tested); that usage is consistently employed in my papers and reviews on the subject entirely independently of Huffman and Kratschmer.

15. In my professional judgement, the above-identified application adequately teaches to the skilled artisan how to make macroscopic amounts of the fullerenes including C_{60} and C_{70}; furthermore, there is ample evidence in the application that

Huffman and Kratschmer had in their possession macroscopic amounts of these products.

16. I have been among those who sought an appropriate name for this family of often co-produced structurally related material and based upon structure and the historical connection with the geodesic dome structures of Buckminster Fuller, I introduced the name of fullerenes for these molecules in 1987 which was later accepted by the scientific community fullerene by about 1990, and this has become the accepted formal name for these materials, e.g., [60] fullerene and [70] fullerene. I refer in particular to the definition I prepared for McGraw-Hill appearing in McGraw Hill Concise Encyclopedia of Science & Technology, 3rd ed. p. 819 (1994).

17. In summary, I am pleased to lend support to the applications of Huffman and Kratschmer for patent protection; as a researcher in the quest for C_{60} I can keenly appreciate the significance of the defining events reflected in the present application; I can, from my own experience, state with confidence that despite our circumstantial evidence of the existence of these molecules, the inevitable speculation and calculations of properties, and our own convictions, given our knowledge at the time, it was by no means predictable nor obvious to one skilled in the art that fullerenes, such as C_{60} or C_{70}, would be recovered in macroscopic quantities by the methods described by Huffman and Kratschmer in the above-identified application, nor to the best of my knowledge, had such results been claimed.

18. I further declare that all statements made herein of my own knowledge are true and that all statements made on information

statements and the like so make are punishable by fine or imprisonment or both under section 1001, Title 18 of United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: 9 June 1995

Harold W. Kroto, Ph. D.

CURRICULUM VITAE

Harold Kroto FRS
Royal Society Research Professor

The School of Chemistry and Molecular Sciences,
The University of Sussex, Brighton, BN1 9QJ, UK

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44 273 606755 University main
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Born 7th Oct 1939 Wisbech, Cambridgeshire, England.

Education

1947-58 Bolton School, Bolton, Lancashire.

1958-61 BSc, University of Sheffield, 1st class honours degree (Chemistry)

1961-64 PhD, University of Sheffield *Electronic Spectroscopy of Unstable Molecules*
Supervisor: R N Dixon FRS (now Professor, Bristol)

1964-65 Postdoctoral Fellow, National Research Council (Ottawa) with D A Ramsay FRS

1965-66 Postdoctoral Fellow, National Research Council (Ottawa) with C C Costain.

1966-67 Member of Technical Staff, Bell Telephone Laboratories, Murray Hill, N.J.
(with Y H Pao, now at Case Western Reserve and D P Santry now at McMaster U)

University Career (University of Sussex 1967-)

1967-68 Tutorial Fellow.
1968-78 Lecturer
1978-85 Reader
1985-91 Professor
1991- Royal Society Research Professor.

Extra-university administration

SRC Millimetre Wave Telescope Sub-Committee 1977-81
SERC Millimetre Wave Telescope Users'Committee 1981-85
SERC Physical Chemistry Subcommittee 1987-90
SERC Synchrotron Radiation Facility Committee 1987-90
SERC Chemistry Committee 1988-91
IAU Sub-group on Astrophysical Chemistry 1987-
MBI Advisory Board of the Max Born Institute (Berlin) 1993-

Meeting (director, organiser or co-orgnaisor)

Brioni International Conferences 1988, 1990, 1993, ...
Royal Society Discussion Meeting 1992
Fullerene Symposium 1993 (Santa Barbara)
Cursos de Verano (El Escorial) *Fullerenos* 1994

Editorial Boards

Chemical Society Reviews 1986- (Chairman 1990-)
Zeitschrift fur Physik D (Atoms Molecules and Clusters) 1992-
Carbon (1992-)
J. Chem. Soc. Chem. Comm. (1993-)

Research Details

University of Sheffield

1961-64 PhD in Free radical spectroscopy by flash photolysis

National Research Council

1964-65 Free radical spectroscopy by flash photolysis
1965-66 Microwave Spectroscopy

Bell Telephone Laboratories

1966-67 Raman Spectroscopy of Liquids, Quantum Chemistry

University of Sussex

1967-72 Free radical spectroscopy/flash photolysis
1967-73 Liquid phase interactions/Raman Spectroscopy
1970- Unstable species/Microwave Spectroscopy
1972-90 Unstable species/Photoelectron Spectroscopy
1976- Interstellar Molecules/Radioastronomy
1983-90 Unstable species/Fourier Transform IR Spectroscopy
1985- Cluster Studies/Carbon, Metals
1990- Fullerene Chemistry, Carbon nanostructures

Temporary Appointments (Visiting Professorships etc)

1974 Visiting Associate Professor, UBC Vancouver (3 months)
1976 Visiting Scientist, NRC Ottawa (3 wks)
1978 Visiting Scientist, NRC Ottawa (3 wks)
1981 Visiting Professor, USC (3 months).
1983 British Council Visitor, Inst Rudjer Boskovic (Zagreb)
1987 CNRS (1 month) Univ Paris Sud (Orsay)
1988- Visiting Professor UCLA (Astronomy)

Extramural Activities

Sport

Tennis and Squash for Sheffield University (1959-1964).
University Athletics Union Finalists - Tennis (1962 and 1963)
President of Athletics Council, Sheffield University (1963-64)

Graphic Art, Design, Television Film

Art Editor *Arrows* Sheffield University Arts Magazine 1962-64
Winner of *Sunday Times* Book Jacket Design Competition 1963
Editor, design and layout of *Chemistry at Sussex*
featured in *Modern Publicity 1979* (international annual of Graphic Design)
Publicity and logos for Chemical Society Meetings
Logo, letterheads for Science and Engineering at Sussex

Publicity, logo, letterheads, poster for BA Meeting 1983
New Scientist BA Advertisement
Logo and letterhead for Inorganic Biochemistry Discussion Group
Logo and letterhead 1990 for *Venture Research International*
(Formerly *BP Venture Research*)
New Cover design and layout for *Chemical Society Reviews*

Chairman of Board of *VEGA SCIENCE TRUST*
Executive producer of five 1-hour Television Films of Royal Institution Discourses for Vega/BBCSelect

Miscellaneous

1981-82	Tilden Lecturer (Royal Society of Chemistry)
1990	Elected Fellow of the Royal Society
1991-	Royal Society Research Professorship
1992	International Prize for New Materials (American Physical Society, R F Curl and R E Smalley)
1992	Italgas Prize for Innovation in Chemistry
1992	Université Libre de Bruxelles (DHC)
1992	University of Stockholm (PhDHC)
1992	Longstaff Medal 1993 (Royal Society of Chemistry)
1992	Academia Europaea (Member)
1993	University of Limburg(DHC)
1994	Hewlett Packard Europhysics Prize (with D R Huffman, W Krätschmer and R E Smalley)
1994	Moet Hennessy*Louis Vuitton *Science pour l'Art* Prize

RESEARCH

Main research areas:

I Spectroscopy of Unstable Species and Reaction Intermediates
(Infrared, Photoelectron, Microwave and Mass Spectrometry)

II Cluster Science
(Carbon and Metal Clusters, Microparticles, Nanofibres)

III Fullerenes
(Chemistry, Physics and Materials Science)

IV Astrophysics
(Interstellar Molecules and Circumstellar Dust)

Research Highlights:

a) Synthesis in 1976 of the first phoaphaalkenes (compounds containing the free carbon phosphorus double bond) in particular $CH_2=PH$ (with N P C Simmons and J F Nixon, Sussex), Refs 1,7.

b) Synthesis in 1976 of the first analogues of HCP, the phosphaalkynes which contain the carbon phoshorus triple bond - in particular CH_3CP (with N P C Simmons and J F Nixon, Sussex), Refs 2,7.

c) The discovery (1976-8) of the cyanopolyynes, HC_nN (n=5,7,9), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, Refs 3,7.

d) The discovery of C_{60}: Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), Refs 8,13,15.

e) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), Ref 9

f) The prediction that C_{60} should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) Ref 10

g) The explanation of why C_{70} is the second stable fullerene (after C_{60}) and the discovery of the *Pentagon Isolation Rule* as a criterion for fullerene stability in general (Refs 11,13,15)

h) The prediction of the tetrahedral structure of C_{28} and the possible stability of "tetravalent" derivatives such as $C_{28}H_4$ Refs 11,15.

i) The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), Refs 12,13.

j) The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C_{60} from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs 14,15.

k) The chromatographic separation/purification of C_{60} and C_{70} and ^{13}C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs 14,15.

PUBLICATIONS

180 research papers. One book "Molecular Rotation Spectra" (Wiley 1975) - reprinted with a new preface by Dover 1992.

Main Publications

1) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospha-alkenes $CF_2=PH$, $CH_2=PCl$ and $CH_2=PH$', *J.C.S. Chem. Comm.*, 513-515 (1976).

2) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne, CH_3CP, by microwave spectroscopy', *Chem. Phys. Letts.*, **42**, 460-461 (1976).

3) A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne, HC_5N', *J. Mol. Spectrosc.*, **62**, 175-180 (1976).

4) L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', *Astrophys. J.*, **205**, L173-175 (1976).

5) H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, 'The Detection of Cyanohexatriyne, HC_7CN, in Heiles' Cloud 2', *Astrophysics J.*, **219**, L133-L137 (1978).

6) N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of HC_9N in Interstellar Space', *Astrophys. J.*, **223**, L105-107 (1978).

7) H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; *Chem. Soc. Revs.*, **11**, 435-491 (1982).

8) H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, 'C_{60}: Buckminsterfullerene', *Nature*, **318**(No.6042), 162-163,(1985)

9) J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, H W Kroto, F K Tittel and R E Smalley 'Lanthanum Complexes of Spheroidal Carbon Shells', *J. Am. Chem. Soc.*, **107**, 7779-7780 (1985).

10) Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley. 'Reactivity of large carbon clusters Spheroidal Carbon Shells and their possible relevance to the formation and morphology of soot', *J. Phys. Chem.*, **90**, 525-528 (1986)

11) H W Kroto, 'The Stability of the Fullerenes C_n (n = 24, 28, 32, 50, 60 and 70)', *Nature* 329, 529-531 (1987)

12) H W Kroto and K McKay, 'The Formation of Quasi-icosahedral Spiral Shell Carbon Particles' *Nature*, 331, 328-331 (1988)

13) H W Kroto "Space, Stars, C_{60} and Soot", *Science*, **242**, 1139-1145 (1988)

14) R Taylor, J P Hare, A K Abdul-Sada, and H W Kroto, "Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70}: The Third Form of Carbon." *J. Chem. Soc. Chem. Commun.*, 1423-1425 (1990)

15) H W Kroto "C_{60}: Buckminsterfullerene, the Celestial Sphere that Fell to Earth", *Angewandte Chemie* **31**, 111-129 (1992)

SYMPOSIUM LECTURES and SEMINARS

Plenary/Invited Lectures

1974	Symp on High Resolution Spectroscopy (Columbus, Ohio)
1976	Symp on Molecular Structure (Austin, Texas)
1978	Faraday Society Spectroscopy Con (Bristol)
1979	14th Internat Free Radical Conf (Sanda, Japan)
	Symposium Interstellar Molecules (Meudon, France)
1980	University College Astronomy Symposium (London)
1981	Conference on Submillimetre Wave Astronomy (London)
	Advances in Spectroscopy, Faraday Meeting (London).
1983	British Association BAYS lecture (x2) (Sussex)
	Federation of Astronomical Socs, Herstmonceux
	RAS Disc Meeting on Interstellar Grains (London)
1984	Symposium on Molecular Structure (Austin, Texas)
	Microwave/IR Spectrosc of Transients (Cambridge)
	EUCHEM Reactive Species in Inorg Chem (Burghausen)
1985	High Resolution Spectroscopy Conference (York)
1986	NATO Workshop PAHs in Space (Les Houches)
	Conference on Molecular Astrophysics (Bruxelles)
	Symp on Planetary Science, Obs. de Paris (Meudon)
	Brioni Conference on Clusters (Brioni,Yugoslavia)
1987	Roy Soc Discussion on The Solar System (London)
	High Resolution Spectroscopy Symp (Dijon, France)
	Roy Soc of Chemistry Autumn Meeting (Nottingham)
	NASA Workshop on Carbon in Space (Ames CA)
1989	Internat Symp on New Aromatic Compounds (Osaka)
	Carbon Conference (Pennsylvania State)
	ACS Conference (Clusters) Miami
	Japan/UK SERC Symposium IMS (Okazaki, Japan)
	Faraday Discussion on Clusters (Warwick)
	6th ISNA Meeting (Osaka)
	Faraday meeting on Clusters (Warwick)
	19th Carbon Conference (Pennsylanvia State Univ)
1990	German Chem Soc Meeting, Organ Chem (Bad Nauheim)
	Solar System Workshop (Clemsen, North Carolina)
	IOP meeting (Warwick)
	Comet Meeting (Bad Honnef Bonn)
1991	4th Chemical Congress of North America (Fuel Science NY)
	6th Symposium on Macrocyclic Chemistry (Sheffield)
	20th Biennial Conference on Carbon (Santa Barbara)
	74th Canadian Chemistry Conference (McMaster, Hamilton)
	IOP Annual Meeting, Low Temperature Physics (Birmingham)
	Rank Prize Workshop on Molecular Cages (Lake District)
	British Association meeting BAYS lecture (Plymouth)
	Mackay Symposium (Birkbeck College)
	IAU Congress Astrochemistry (Campos de Jordao, Brazil)
	Swedish Physical Society (Stockholm)
	Fullerene Workshop (RISU, Roskilde, Denmark)
	Condensed Matter Physics 1991 (CMMP 91, Birmingham)
1992	Workshop on Atoms and Clusters 92 (Atami, Japan)
	Symp. on Atomic and Molecular Structure (Trentino)
	Portuguese Chemisty Society Meeting 1992 (Lisbon)

1st Italian Fullerene Conference (Bologna, Italy)
IOP meeting on Fullerenes (Rutherford Lab)
Universite Libre de Bruxelles Conference (Belgium)
Pittcon 92 Conference (New Orleans, USA)
American Physical Society meeting (Indianapolis)
Leermaker Symposium (Wesleyan U, Conn, USA)
Infrared Astronomy Conference (Calgary, Canada)
Adriatico Conference on Clusters (Trieste, Italy)
Invited Lecturer Cursos de Verano 92 (El Escorial)
European Materials Res Soc Meeting (Strasbourg)
IOP/RSC Joint Symposium on Fullerenes (London)
Vacuum Ultra Violet Meeting (VUV10, Paris)
11th Canadian Theoretical Chem. Conf. (Montreal)
12th Conf on Chemical Education (UCDavis, USA)
23rd European Conf, Mol Spectros (EUCMOS23, Vienna)
Symposium fur Theoretische Chemie (Blixen, Italy)
Gordon Conference on Clusters (Irsee, Germany)
Italgas Chemistry Prize Lecture (Turin)
University of Helsinki (Spec Lect) (Finland)
Gordon Combustion Conf (Spec Lect) (Hawaii)

1993 Italian Fullerene/Superconductivity Meeting - Pisa
Croatian Chemical Society Symposium - Zagreb
Fullerene/Superconductivity Meeting - Kirchberg
ACS Meeting (Fullerenes) - Denver
Sydney Leach Symposium - Paris
Theoretical Symposium - Namur
NATO Fullerene Workshop - Crete
Centenary Conf of Norwegian Chemical Society - Oslo
Fullerenes 93 Symposium - Santa Barbara
IURCAM Conference - Tokyo
Solid State Devices Conference - Tokyo
Span/American Inorg Chem Conf - Santiago (Spain)
Brioni International Conference - Brioni
Materials Conference - Wroclaw (x2)
Spanish Materials Conference - Oviedo
ACOLS Conference - Melbourne (x2)
London Schools Science Symposium

1994 Association of Science Education Conference (Birmingham)
New Organic Materials Conference (Madrid)
Science Research Institute Inaugural Meeting (Salford)
Student Chemical Society Centenary Meeting (Sheffield)
Berzelius Dagarna (Stockholm)
European Physical Society - Hewlett Packard Prize Lecture (Madrid)
Sussex University Science Teachers Conference (Sussex)
World Affairs Conference (Boulder, Colorado) (x2)
Cluster Workshop (Ameland, Netherlands) (x4)
3rd Workshop on Advances in Phys Chem (Nanjing, China)
Cursos de Verano Fullerene Workshop (El Escorial, Spain)
LVMH Science pour l'art Prize lecture (Paris, France)
Gordon Conference (Ceramic Materials) New Hampshire (special lecture)
Materials Research Soc Meeting (Boston)

Named/Special Lectureships

1992 Probst Lecture - Southern Illinois Univ (USA)

1993 Cherwell-Simon Lecture (Oxford)
Steinhofer Lecture (Kaiserslautern)

Dreyfus Lecture (UCLA)
John Coffin Memorial Lecture (University of London)
30th Anniv Lecturer (Chinese Univ of Hong Kong)

1994 Brode Lecturer (Whitman College, Washington, USA)
Winegard Lecturer (Guelph University, Ontario, Canada)
Kolthoff Lecturer (University of Minnesota, USA)
Rayleigh Lecturer (Harrow School
Chemical Inst of Canada Lecturer (Sherbrook University, Quebec, Canada)
Distinguished lecturer (University of Kentucky, Center for Applied Energy Research)

1995 Werner Lecturer (Trinity College, Dublin)
Tizard Lecturer (Westminster, School)

Research Seminars (Overseas)

1974 Bell Telephone Labs (NJ), NRC (Ottawa), UBC (Vancouver)
1976 Paris Sud (Orsay), Harvard, NRC (Ottawa)
1977 Lille, Brussels, Montreal, Waterloo
1978 Cal. State (L.A.), Cal Tech.(Pasadena), Arizona (Tucson), USC(Los Angeles), Herzberg Institute (NRC, Ottawa), UC Berkeley
1979 UBC (Vancouver), Montreal
1980 IBM (San Jose), UC Santa Barbara, USC (Los Angeles), Chemical Society Zurich
1981 UC Berkeley
1982 Trinity College (Dublin), NRC. (Ottawa)
1983 Basel, Kiel, Giessen, Inst.Rudger Boskovic (Zagreb)

1985 ETH (Zurich), Basel, Inst. R. Boskovic (Zagreb), Rice Univ. (Houston), Texas A&M, Texas Tech.

1986 Harvard, Guelph-Waterloo, Aachen (Tech Hochschule), Chicago

1987 USC (Los Angeles), UCLA (Astron), Berkeley, JPL (Pasadena)

1988 UCLA(Chem), Stanford, Arizona(Tucson), Arizona State (Tempe), Tech. Hochschul (Darmstadt), Max Planck Inst (Martinsried)

1989 MPI (Munich), UCLA(Chem), Oregon, JPL(Pasadena), Berkeley, NASA (Moffett Field), Toronto, Montreal, Guelph.

1991 California (Los Angeles, UCLA), California (Berkeley), Cal Tech (Pasadena), California (Santa Barbara, UCSB), Belo Horizonte (Brazil), Recife (Brazil), Erlangen, Freigburg, Heidelberg, Shell (Amsterdam), NIST (Washington) NRC (Ottawa), Arizona(Tucson)

1992 Pisa (Italy), Michigan (Ann Arbor, USA), Chicago (USA), McGill (Montreal, Canada), Chemical Society of Zurich, Laue Langevin Laboratory (Grenoble), Aarhus (Denmark), Helsinki (Finland), Niels Bohr Inst(Copenhagen), Stockholm (DHc lecture), Tokyo (Japan), Shinshu (Nagano, Japan), Kitagawa Industries (Tokyo Japan), Nobeyama Radio Observatory (Japan), NRC (Ottawa, Canada)

1993 Basel Chemical Society, ULB Bruxelles (DHC lecture), Josef Stefan Institute (Ljubljana), Limburg (DHC lectures), UC San Diego, Crete, NEC Japan, Shinshu, Shizuoka, Materials Institute (Warsaw), Milan, Berlin Chemical Society

1994 2xRSC (Belgium section) lectures (Brussels) (1 British School), Swedish Royal Academy (Stockholm), Stockholm University (Physics Dept), Herzberg Inst NRC Ottawa, Braunschweig, Scherring (Berlin), Humboldt Univ Berlin, Bielefeld, KFA (Julich), Peking U x2 (Beijing), Bell Labs NJ, UNAM Mexico City, UCLA (Astronomy)

1995

UK Research Seminars (* > 1)

Sussex (Chemistry, Physics, Astronomy, Biology*), Cambridge* (Chemistry and Astronomy Depts), Southampton*, Oxford*, Reading*, Nottingham*, Sheffield*, Warwick*, Glasgow, Strathclyde, East Anglia, Coleraine, Manchester*, Edinburgh*, Birmingham*, U.C. London* (Chemistry and Astronomy), Bristol*, ICI*, Surrey.

UK General Lectures for Students and Public (Chemistry/Astronomy)

Southampton*, Reading*, Sussex*, Exeter*, Bristol*, Bath, Surrey, Essex, Imperial College*, University College*, Cardiff*, Kent, Swansea, U.C.North Wales, Portsmouth, Leicester*, Loughborough, Thames, Durham, Leeds*, Nottingham*, Open University, Cambridge*, RSC (Sheffield) RSC (Cumberland), Brighton Astron. Soc.*, Eastbourne Astron.Soc., Croydon Astron. Soc., Alembic Club (Oxford), U.C. Sussex(Astron, Biology) Q.M.C*. Sussex Town and Gown, Mid-Kent Astronomy Society, Royal Institution (Friday Evening Discourse), East Midlands RSC.

1993	Bath, Cambridge, Imperial College, Birmingham, Warwick Royal Society, Nottingham, Liverpool, Pfizer Company,
1994	Leicester, Aston, Royal Institution (Friday Evening Discourse (#2)), Sussex, East Anglia, Surrey
1995	Durham, Liverpool, Queen's (Belfast), Coleraine

Schools'Lectures

Christ's Hospital School, Worthing Sixth Form College, Kingston Polytechnic (Schools Lecture), RSC Schools L RSC Essex Schools Lecture, Chelsea College, Charterhouse, London Schools (Q.M.C.), King's School Canterbury, St Dominics 6th form College Harrow, Dreyfus Schools' Lectures, 1986 at RoyalInstitution, St Paul's School for Girls Open Day Lectures (Sussex), Hurstpierpoint College BAYS Lecture(Southampton)

BROADCAST INTERVIEWS etc

1976	BBC Radio (Science Now) "Interstellar Chains"
1977	BBC Radio World Service "Interstellar Chains"
1979	BBC TV OU Film based on my lecture "Chemistry between the Stars"
1985	BBC Radio World Service "Chemistry in Space"
1985	BBC Radio Sussex "Chemistry in Space"
1986	BBC (Science Now) "C60,Buckminsterfullerene"
1989	USA Local Radio Carbon in Space)
1991	BBC Radio programme - "Science Now"
1992	BBC Radio World Service (x2)
1992	BBC TV "Molecules with Sunglasses" Horizon
1992	RAI TV Interview for Italian Television (Premio Italgas)
1992	NDR TV Nord Deutsche Rundfunk Programme on Fullerenes
1993	SFB Radio - Sender Freies Berlin, Radio
1993	UCLA video film Dreyfus Lecture
1994	BBC Select TV - Royal Institution Lecture

RESEARCH GRANTS

1970	Microwave Spectroscopy	(SRC)	10 000
1974	Microwave Spectroscopy	(SRC)	24 000

1974	Microwave Spectroscopy	(Sch)	10,000
1978	Photoelectron Spectroscopy (with M F Lappert)	(SRC)	18,000
1979	Computer	(SRC)	20,000
1977	PDF (with J F Nixon)	(SRC)	18,000
1977	Astronomy (with T Oka)	(NATO)	2,500
1981	Infra Red Spectroscopy	(SERC)	72,000
1980	Quad Mass Spectrometer	(RS)	5,000
1983	IR spectroscopy	(SERC)	20,000
1986	Jet Cooled i.r.spectroscopy	(SERC)	33,000
1987	Clusters (with A J Stace)	(SERC)	157,000
1992	Fullerene Chemistry with R Taylor/ D R M Walton	(BP/ICI/SERC)	200,000
1992	Cluster Rolling Grant with AJ Stace/J N Murrell)	(SERC)	300,000

MAIN RESEARCH COLLABORATION

The value of microwave and photoelectron techniques to a wide area of chemistry has been highlighted by fruitful collaboration with colleagues here at Sussex. One important research project carried out with D R M Walton involved the synthesis and study of long chain polyynes. This work led to our detection this species in interstellar space by Radioastronomy carried out with T Oka and astronomers at the Herzberg Institute for Astrophysics, NRCC Ottawa. A project, carried out with J F Nixon has opened up a new field of organophosphorus chemistry. Work has been carried out in collaboration with J P Maier (Basle) to study the ions of unstable molecules is now in progress. Cluster Beam studies on Carbon with R F Curl and R E Smalley (Rice). Astronomy Research has been carried out with M Jura at UCLA. The present Sussex Programme on Fullerene Chemistry is being carried out in collaboration with R Taylor and D R M Walton.

ASSOCIATED RESEARCH PERSONNEL

35 D.Phil students,
10 Chemistry by Thesis students
12 Postdoctoral Fellows.

POPULAR PRESS COVERAGE

Interstellar Molecule Discoveries,

Ottawa Citizen, The Times, The New York Times, New Scientist, Scientific American

Unstable Phoshorus Molecules:

New Scientist

Fullerenes

New York Times (x2), The Daily Telegraph, Houston Chronicle, New Scientist, C&E News, Omni, Sky and Telescope, Science Now, Economist, Der Spiegel, Time, Daily Telgraph.....

TEACHING EXPERIENCE

Lecture Courses (Sheffield University)

(1961-1963) taught O-level Chemistry at Sheffield Technical College

Lecture Courses (University of Sussex 1968-)

Chemistry Highlights Lectures for Freshers
1st and 2nd year Spectroscopy courses
Structural Methods (2nd year course)
Symmetry (2nd year)
Advanced Structure (3rd year course)
Valence Theory for Biochemists (2nd year course).
Rotational Spectroscopy (3rd year option)
Astrophysical Chemistry (3rd year option)
Topics in Chemical Physics (3rd year course)
High resolution Techniques (graduate course)

Lecture Courses (Univ. of Southern California, Los Angeles, 1981)

Chemistry & Spectroscopy of Interstellar Molecules

Seminars and Tutorials (Sussex)

Atomic and Molecular Structure (1st year course).
Mechanistic Principles (1st and 2nd year courses).
Thermodynamics (1 year course).
Conceptual Models (3rd year option course).
Synthesis (1st year course).
Statistical Mechanics

Practical Courses (Sussex)

1st year Introductory Practical Chemistry
2nd year Physical Chemistry (organiser 1978-80)
3rd year Chemistry and Chemical Physics Projects.

ADMINISTRATIVE POSITIONS

University of Sussex

Chairman of the University Safety Committee (1986-7)
School Undergraduate Admissions Organiser (1973-1976).
Chemistry by Thesis Sub-Board (1975-1978), Sec (1976-78).
Chemical Physics Subject Group, Secretary (1974-76), Chairman (1976-82 85-87).
Chemical Physics Sub-Board, Secretary (1974-76) Chairman (1979-83, 85-87)
School Joint Committee (1973-74, 77), Chairman (1974)
White House Careers Weekend (Weekend Residential Seminar Course on Careers for 3rd year students), Organiser (1974)
Editing, design and layout of "Chemistry at Sussex" School, Teaching and Research Handbook (copy available). The cover design was reproduced in "Modern Publicity", a major international annual of the best in graphic art and design
School Chemical Society Lecture Organiser (1987-)
University Senate (1979-1980).
Science Committee (1980, 1981-2, 1985-7)
Laboratory Director (1983-86): Overall responsibility for Tech Staff logistics, deployment, grading etc; School research strategy, budgeting, expenditure, building and laboratory space allocation.

Chem. Rev. 1991, 91, 1213–12

C_{60}: Buckminsterfullerene

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School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Received May 2, 1991 (Revised Manuscript Received July 26, 199

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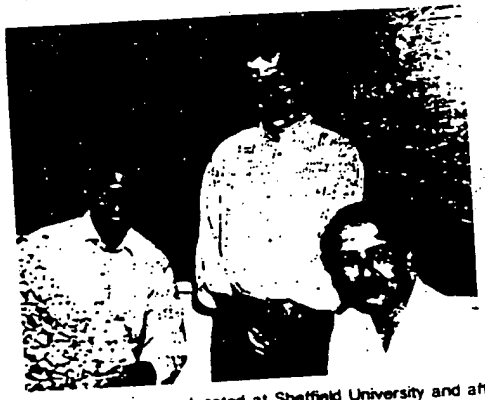

Harry Kroto (left) was educated at Sheffield University and after periods at the National Research Council, Canada (1964–1966), and Bell Telephone Laboratories (1966–1967) went to the University of Sussex where he is now Professor of Chemistry. His research into the production and spectroscopic characterization of new species such as the phospahaalkenes, phospahaalkynes, thiocarbonyls, and polyynes led, via radioastronomy studies of interstellar molecules, to carbon cluster beam experiments aimed at understanding stellar chemistry. Wahab Allaf (right) who was educated at Aleppo University (Syria) and Sussex University is carrying out research on carbon clusters and laser chemistry. Simon Balm (center) who is studying cluster beam reactions and astrophysical chemistry was educated at Durham University and Sussex University.

I. Introduction

In 1967 Palmer and Shelef wrote the definitive review of the early work on carbon clusters in their article on the composition of carbon vapor.[1] Major advances have however been made in the interim period, and the overall situation has been updated by Weltner and Van Zee[2] who have given a very complete picture of the state of this fascinating field. Although Weltner and Van Zee's review is comprehensive (up to Nov 1, 1988), covering all aspects of carbon cluster properties, recent advances in the story of C_{60} buckminsterfullerene (Figure 1) indicate that a specialized review is necessary and timely. The existence of the fullerenes as a family has now been established and it is useful to use a convenient nomenclature such as fullerene-60 or fullerene-70 which can apply to the whole family. There are of course numerous possible C_{60} and C_{70} cage isomers, however here we shall, in general, mean the most geodesically stable cages for which there is now no doubt in the case of the 60 and 70 atom species—they are (I_h)fullerene-60 and (D_{5h})fullerene-70 where standard symmetry labels have been added as prefixes. Since the existence of fullerene-60 and its spontaneous creation have ramifications in numerous areas from the properties of carbonaceous solids and microparticles through combustion, thermolysis, and synthetic organic chemistry to the nature of the carbonaceous constituents of space, these implications are also surveyed.

During a series of experiments in 1985 which probed the nature and chemical reactivity of the species produced during the nucleation of a carbon plasma the C_{60} species was discovered to be stable by Kroto, Heath, O'Brien, Curl, and Smalley.[3] It was proposed that this stability was due to geodesic and electronic properties inherent in the truncated icosahedral cage structure shown in Figure 1 and the molecule was named buckminsterfullerene. This novel proposal did not receive instant universal acceptance since it appeared to have been based on highly circumstantial evidence. Indeed it is now clear that there was a significant degree of scepticism in the minds of some with regard to the validity of the proposal, perhaps because the evidence was dispersed among many disparate scientific observations, much like the way that C_{60} itself may—we now realize—be involved in many processes involving carbon in the environment and space. However, systems giving rise to C_{60} were subjected to many detailed investigations subsequent to the discovery paper,[3] and some important points evolved which are worthy of highlighting:

(i) A wealth of convincing experimental evidence was amassed that showed that C_{60} possessed unique physicochemical stability—a conclusion totally independent of the cage structure proposal.

(ii) The fullerene cage proposal was the simplest and most elegant explanation of the unique behavior and no serious alternative explanation was ever presented.

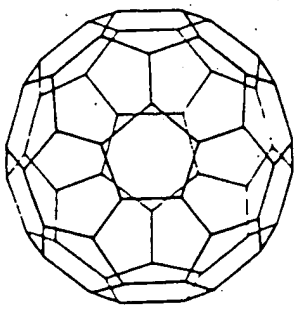

Figure 1. C_{60} buckminsterfullerene.[1]

(iii) The proposal was consistent with many earlier observations on bulk carbon and clarified some previously unexplained phenomena in carbon chemistry.

The fullerene structural proposal has recently been confirmed by complementary observations from two groups. Krätschmer, Lamb, Fostiropoulos, and Huffman,[4] in following up their earlier IR investigation (in 1989)[5] which suggested that C_{60} might be present in arc-processed graphite, extracted a soluble material which formed crystals. The X-ray analysis showed the material to consist of 10-Å diameter spheroidal molecules and supplementary mass spectrometric and infrared data provided the first unequivocal evidence for C_{60} (and C_{70}). In a parallel, independent investigation which probed this same original key observation,[5] Taylor, Hare, Abdul-Sada, and Kroto[6] found that similarly arc-processed graphite gave rise to a 720 mass peak, commensurate with the presence of fullerene-60, and that this material was soluble and could be extracted directly. The extracted C_{60} compound yielded a single ^{13}C NMR line which proved that all 60 carbon atoms are equivalent as expected for the truncated icosahedral buckminsterfullerene structure. Taylor et al. also showed that C_{60} and C_{70} can be separated chromatographically and that the latter has the D_{5h} prolate, ellipsoidal structure first suggested by Heath et al.[6] These results provide further support for the conjecture that a whole family of fullerenes exists.[7,8]

Since these revelations, which are discussed further in section IX, the fullerene field has exploded and numerous groups are probing various facets of physicochemical properties of the fullerenes. Indeed a new field of carbon chemistry has been born, and the first faltering steps of the promising infant are described in section X. Thus this review is particularly timely as it is written at the precise moment when the final sentence in the last paragraph of the *first* chapter in the story of the fullerenes has been completed. The opening paragraphs in the next chapter are just being written and they herald a new era in which the flat world of polycyclic aromatic chemistry has been replaced by a postbuckmisterfullerene one in which round structures are favored under certain surprisingly common circumstances.[10] This article reviews the buckminsterfullerene story from the time when it was just a twinkle in the eyes of a few imaginative theoreticians, through the experiments which revealed that it actually formed spontaneously and exhibited stability to the most recent revelations that it could be isolated and did indeed possess the round hollow cage structure as proposed. As many contributions to the story as could be traced by Dec 1990 are included.

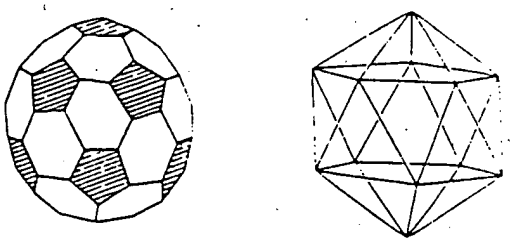

Figure 2. Diagram of C_{60} next to an icosahedron published in the book *Aromaticity* by Yoshida and Osawa.[14] These authors discuss (in Japanese) the "superaromaticity" which might accompany electron delocalization over a three-dimensional truncated icosahedral pure carbon molecule.

II. Summary of Relevant Carbon Studies Prior to the Discovery of C_{60} Stability

At least part of the reason for the degree of interest engendered by the buckminsterfullerene proposal revolves around its high degree of symmetry. Mankind has always been fascinated by symmetric objects, indeed stone artifacts with the form of the Platonic solids, dating back to neolithic times, have been found in Scotland,[11] indicating that human beings have long had a spiritual affinity with abstract symmetry and an aesthetic fascination for symmetric objects. The truncated icosahedron is one of the Archimedian semiregular *solids*; however in *hollow* form an early example appears in the book *De Divina Proportione* by Fra Lucia Pacioli. A reproduction of this drawing by Leonardo Da Vinci entitled "VCOSEDRON ABSCISVS VACVVS" is to be found in the book *The Unknown Leonardo*,[12] which is rather more accessible than the original!

The C_{60} molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 1970[13] and discussed further in a chapter on "Superaromaticity" in a book by Yoshida and Osawa[14] in 1971; the original diagram is depicted in Figure 2. An equally imaginative article, which actually predates this work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages.[15,16] The next paper was that of Bochvar and Gal'pern in 1973 who also published a Hückel calculation on C_{60}.[17,18] In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for fullerene-60.[19] Davidson's orbital energy level diagram, depicted in Figure 3, was determined by using a calculator, and this paper contains an unusually prescient paragraph in the light of recent observations (particularly those in section VII): "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three-dimensional aromaticity." Haymet's study[20] on this molecule coincided very closely with its discovery in 1985.[3]

On the experimental front there were many very important early papers on carbon clusters and these have already been reviewed.[1,2] Perhaps the most interesting early carbon cluster papers (and the ones which in fact actually stimulated the discovery experiments) were

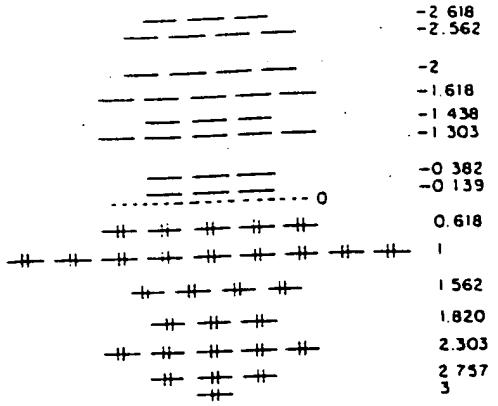

Figure 3. The Hückel molecular orbital calculation for buckminsterfullerene was carried out by Bochvar and Gal'pern[17,18] (1973) and Davidson[19] (1980), prior to, and by Haymet[20] (1985) coincidentally with, its discovery. The orbital energy level diagram (units of β) depicted here is that published by Davidson[19] who determined it using graph theory to obtain simplified algebraic relations which were evaluated with a calculator (reprinted from ref 19; copyright 1981 Springer-Verlag Publishers).

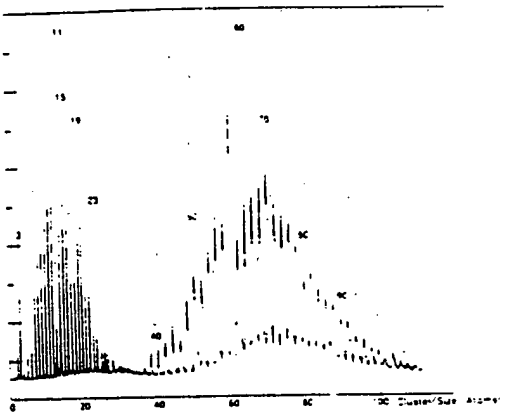

Figure 4. Time-of-flight mass spectrum observed by Rohlfing, Cox and Kaldor,[25] of carbon clusters produced by laser vaporization of graphite. In this experiment carbon clusters with 30–190 atoms were detected for the first time. These studies showed that only even-numbered clusters were stable (reprinted from ref 25, copyright 1984 the American Institute of Physics).

those published by Hintenberger and co-workers in 1959–63[21-24] in which it was shown that species with up to 33 carbon atoms could form in a carbon arc. The next important advance was made by Rohlfing, Cox, and Kaldor[25] in 1984 who found that much larger carbon clusters (C_n with n = 30–190) could be produced by vaporization of graphite (Figure 4). Rohlfing et al. used the supersonic nozzle, laser vaporization technique developed by Smalley and co-workers at Rice University[26] in 1981. In this technique clusters are made by laser vaporization of refractory materials into a pulse of helium or argon in the throat of a supersonic nozzle. The vaporized material nucleates in the gas pulse which then expands supersonically into a vacuum chamber where it cools and is skimmed. The skimmed beam passes into a second chamber where the entrained clusters are ionized by a second laser pulse and the cluster ion mass distributions determined by time of flight mass spectrometry (TOF-MS). The mass spectrum observed by Rohlfing et al.[25] is shown in Figure 4; they pointed out that only ions with *even* numbers of carbon atoms were observable for the new family of clusters with more than 30 carbon atoms. Packing or magic number effects are very weak under these conditions.[27] Bloomfield et al.[28] also studied carbon clusters by the same technique and observed both positive and negative *even* numbered ions. They also studied the fragmentation behavior of the new family and in particular chose the C_{60} cluster for further study and showed that it could be photodecomposed with 532-nm multiphoton laser radiation.

III. The Discovery of C_{60}: Buckminsterfullerene

In September 1985 the reactions of carbon clusters were investigated by the Rice/Sussex group.[3,29,30] These experiments were aimed at simulating the conditions under which carbon nucleates in the atmospheres of cool N-type red giant stars. Circumstantial evidence appeared to suggest[31,32] that such stars might be likely sources of the long carbon chain molecules in the interstellar medium and in particular that the formation process might be related in some important way to soot formation.[33] The interstellar cyanopolyynes (HC_nN n = 5–11)) were discovered by a synergistic combination of laboratory microwave spectroscopy experiments,[33,34] theoretical analysis,[35] and observational radioastronomy.[36-39] The cluster beam experiments showed convincingly that species such as HC_7N and HC_9N, which had been detected in space,[36-38] could be produced by such laboratory simulations of the conditions in carbon stars.[29,30] A second motivation for probing laser vaporization of graphite was the question of whether carbon clusters were associated with the so-called diffuse interstellar bands as Douglas had proposed in 1977.[40] The development of resonant 2-photon ionization in conjunction with the cluster beam technique to obtain the high-resolution spectrum of SiC_2 by Michalopoulos et al.[41] suggested that the electronic spectra of carbon clusters might be accessible by this technique. During the course of the experiments[29,30] which probed the behavior of the pure carbon clusters a striking discovery was made—under some clustering conditions the 720 mass peak appeared to be extremely strong (Figure 5).[3] Indeed the intensity of the C_{60} peak, relative to the adjacent cluster distribution, could be varied dramatically just by altering the conditions. In particular, conditions could be found for which the mass spectrum was totally dominated by the C_{60} peak—at least in the mass range accessible (Figure 6). It was concluded that C_{60} must be particularly stable to further nucleation and it was proposed that this might be explained by the geodesic factors inherent in a truncated icosahedral cage structure in which all the atoms were connected by sp^2 bonds and the remaining 60 π electrons distributed in such a way that aromatic character appeared highly likely.[3]

In these experiments it was found that the C_{70} peak also showed clear enhancement although to a lesser extent; the C_{60}/C_{70} ratio was ca. 5/1 in general. In previous experiments[25,27,28] the $C_{60}/(C_{58}$ or $C_{62})$ ratio was ca. 2/1 (Figure 4) whereas in the new experiments

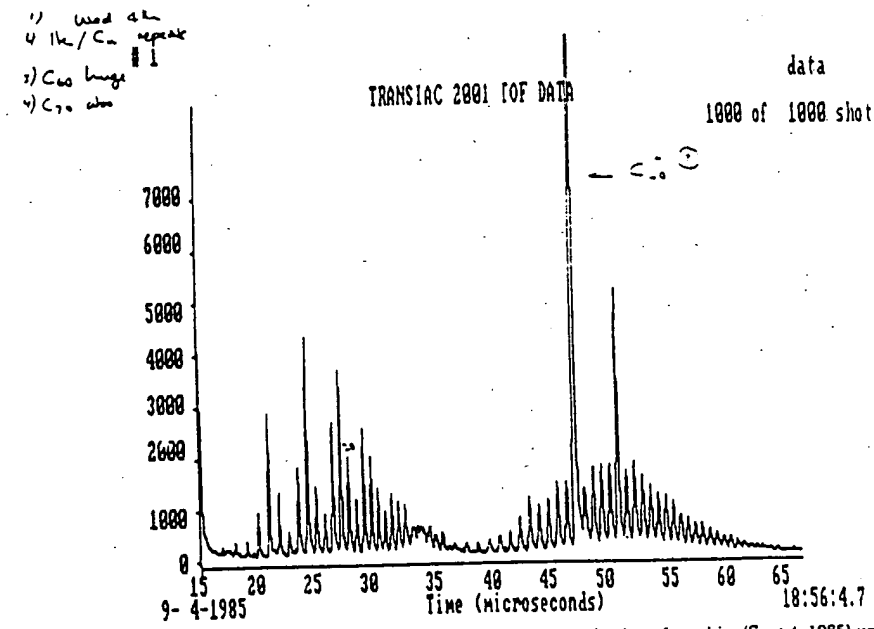

Figure 5. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite (Sept 4, 1985) under conditions which first exhibited the dominance of the C_{60} cluster and led to the recognition that 60 might be a "magic" number.

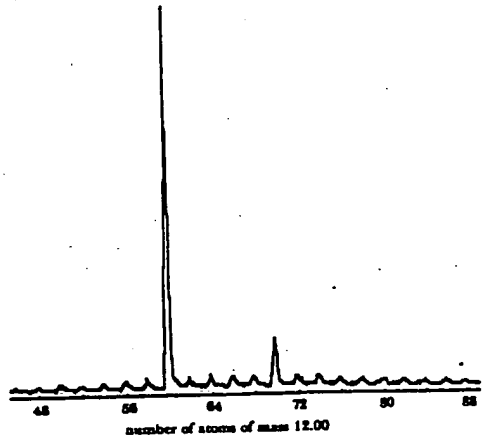

Figure 6. Time-of-flight mass spectrum carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant C_{60} cluster signal.[3] Note also the prominence of C_{70}.

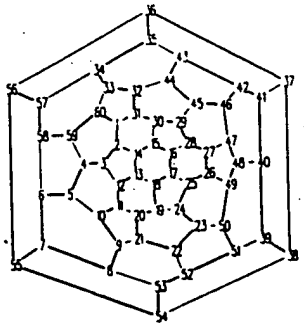

Figure 7. The IUPAC name of fullerene-60 determined by computer analysis—according to P. Rose.[47]

conditions were found in which a ratio of 20/1 or more was achieved (Figure 6). It was soon realized that although C_{60} generally appeared fairly special, the conditions under which it appeared dominant were rather unusual. They were conditions in which the major fraction of the carbon had nucleated to form macroscopic particles too large to be detectable by the mass spectrometer. Thus it was recognized that the signal shown in Figure 6 shows the "small" carbon species which remain when the microparticles have formed. Due to the fact that geodesic structural concepts were a guide to the hollow cage structural explanation that

cule was named after Buckminster Fuller, the inventor of the geodesic domes.[43] Although the name chosen, buckminsterfullerene[3,44] is a little long,[45,46] it is not as long as the IUPAC alternative and not as difficult to pronounce (Figure 7)[47] and certainly not as difficult to derive![48,49] The name fullerene can be conveniently and appositely used for the whole family of closed carbon cages with the 12 pentagons and N (other than one) hexagons in an sp^2 network.[8,44] For several reasons, not least the problem of ambiguity with international sports nomenclature, some other names are probably not as satisfactory; they are certainly less enlightening.

Since the buckminsterfullerene detection paper[3] was

work has been carried out. Two complementary accounts covering many of the important general implications and experimental observations have been given by Kroto[50] and Curl and Smalley.[51] More-focused accounts have also been published dealing mainly with experimental observations,[52-54] astrophysical implications,[42,55-58] symmetry and structure considerations of fullerene-60, and the icosahedral giant fullerenes.[59,60] The chemical implications have also been discussed by Kroto[61] and Kroto and Walton.[10] Hirota[62] and Heath[63] discuss fullerene-60 as well as other novel carbon molecules.

IV. Sources of C_{60}

In the original work, which showed how conditions could be achieved to produce a signal in which the C_{60} peak was dominant, the pulsed nozzle/laser vaporization technique[26] was used to produce the clusters from a graphite target and photoionization TOF-MS used to detect them. The laser-produced plasma expanded into a high pressure (ca. 1–10 atm) of He and the target graphite surface was continually replenished so that the surface remained essentially flat. A nozzle extender was used to increase the clustering time prior to expansion to ca. 100 μs and the high He pressure increased the nucleation rate. Although initially it was conjectured that perhaps graphitic sheet fragments might have been ablated from the graphite target and rearranged into the buckminsterfullerene structure, subsequent considerations suggested that C_{60} was more likely to have formed by nucleation from carbon vapor consisting, at least initially, of C atoms and very small carbon molecules.[52] Negative ion distributions produced by crossing a laser with the cluster beam just as it exited the nozzle[64] have been studied, and the relationship between these and positive and negative ion distributions, obtained directly from the vaporization zone (i.e. without photoionization), has been discussed by Hahn et al.[65] and O'Brien et al.[66] The consensus of opinion was that C_{60} appeared to exhibit special behavior whether charged (positive or negative) or neutral and that the nucleation rate order was neutrals > cations > anions.[66] Very detailed discussion of the conditions under which C_{60} appears to be special has been given by Cox et al.[67] These studies are discussed in more detail in section V.

Carbon cluster distributions exhibiting dominant C_{60}^+ signals, can be produced in another way as O'Keefe, Ross, and Baronavski[68] and Pradel et al.[69] have shown using high vacuum TOF-MS. In these experiments the graphite target is inside the mass spectrometer vacuum system and remains stationary. After several laser pulses a hole is drilled in the graphite and nucleation appears to occur in the cavity. McElvany et al.,[70] using ICR-MS techniques, have shown that if the axis of the laser-drilled hole is aligned parallel to the trapping magnetic field a strong C_{60}^+ signal predominates in the mass spectrum. In a study of the small cluster distribution, McElvany, Dunlap, and O'Keefe[71] found that the vaporization of a diamond target produces the same distribution as does graphite. This result indicates that the clusters appear to be produced by nucleation of atomic/molecular carbon vapor rather by a process involving the ablation of bulk fragments from the target. Meijer and Bethune[72] have modified the original laser

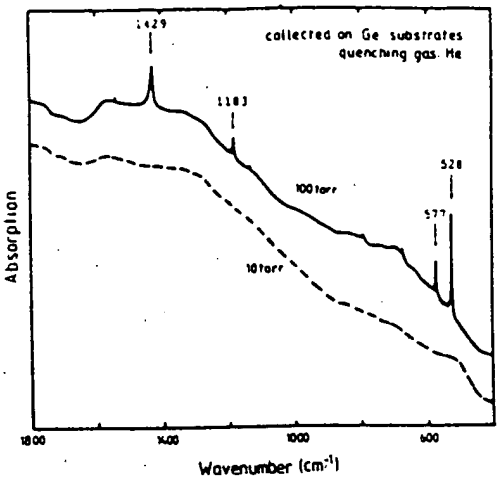

Figure 8. Infrared absorption spectrum observed in 1989 by Krätschmer, Fostiropoulos, and Huffman[5,74] from carbon produced by arc-discharge processing. Krätschmer et al. made the perceptive observation that the four sharp absorption features indicated might belong to fullerene-60. The frequencies were tantalizingly consistent with theoretical predictions (section VIII) for the fundamental vibrations of fullerene-60 (reprinted from ref 74; copyright 1990 Elsevier Science Publishers).

vaporization procedure for producing C_{60}[3] in order to deposit material on a film. They have shown that the mass spectrum obtained by subsequent laser desorption of the resulting material yields a very similar cluster distribution to that of the cluster beam experiments. They have also carried out isotope scrambling measurements[73] supporting the conclusion that C_{60} is assembled from small carbon species in the gas phase after vaporization (see section VI).

A fascinating and ultimately key observation was described in September 1989 by the Heidelberg/Tucson group: Krätschmer, Fostiropoulos, and Huffman[5,74] who detected four weak bands in the infrared spectrum of a film deposited from a carbon arc under argon (Figure 8). Krätschmer et al. pointed out that the vibrational frequencies of the four bands (and associated ^{13}C shifts) observed were in tantalizingly close agreement with theoretical estimates for fullerene-60 (details in sections VIII and IX).

Several other interesting studies have shown that laser vaporization of a wide variety of carbonaceous target materials (other than *pure* carbon) also yields a dominant C_{60} signal: e.g. carbon films (Creasy and Brenna[75]), polymers such as polyimides (Creasy and Brenna,[76] and Cambell et al.[77-79]), coal (Greenwood et al.[80]), polycyclic aromatic hydrocarbons (Giardini-Guidoni et al.,[81] and Lineman et al.[82,83]). Last but not least, So and Wilkins[84] have shown that C_{60} can be detected by laser desorption of soot! In fact they have observed even-numbered carbon clusters with as many as 600 carbon atoms (Figure 9). This result and similar experiments may indicate that giant fullerenes may also be forming.[60] All experiments show that conditions can be found in which the C_{60}^+ peak is either prominent or dominant. However conditions also exist for which this is not the case.[84] It is likely that the availability of many other pathways to "organic" (H-containing species) may be responsible for some of the latter observations.

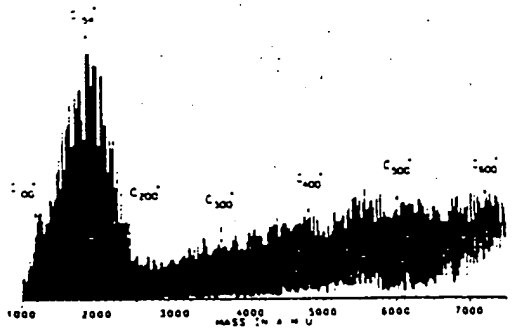

Figure 9. Laser desorption Fourier transform mass spectrum, observed by So and Wilkins,[84] of soot deposited on a KCl-coated stainless steel probe tip. Note that *all* the peaks here also correspond to *even* numbered carbon species. Since only even-numbered carbon aggregates can close perfectly it is possible that the explanation for this phenomenon is that these species are fullerenes and that the larger species are giant fullerenes of the kind depicted in Figure 22.

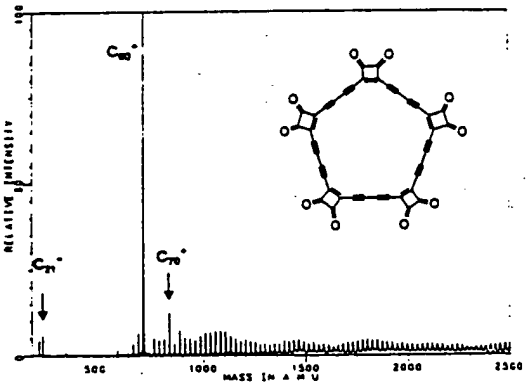

Figure 10. Remarkable positive-ion laser desorption Fourier transform mass spectrum, observed by Rubin et al.,[85] of the ring carbon oxide depicted under low laser power. This oxide which might be expected to decarbonylate to yield a C_{30} monocyclic ring has clearly dimersed to form C_{60} buckminsterfullerene!

A most exciting result was described by Rubin et al.[85] who have used a combination of organic synthesis and laser desorption mass spectrometry. In a preliminary study by the same group (Diederich et al.[86]) attempted to prepare pure carbon rings, a prominent peak for the C_{18} cluster was detected during mass spectrometric analysis of a laser desorbed 18-carbon ring precursor. This work has now been advanced in spectacular fashion; refined measurements on C_{18} and C_{24} precursors[85] yield mass spectra which show prominent C_{60} and C_{70} signals. However most striking is the observation that laser desorption of the C_{30} ring precursor produces a mass spectrum containing a totally dominant C_{60} signal! (Figure 10). This result suggests that, in the vapor phase, a spectacular dimerization process occurs in which two C_{30} polyyne/cumulene rings combine in a concerted folding rearrangement to form the C_{60} cage.[10] The implications of this process and indeed other aspects of the fullerene discovery for organic chemistry have been considered.[10,61]

Some of the most important of all these experiments were those of Homann and co-workers[87-90] who detected

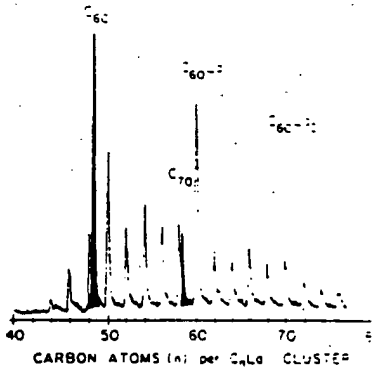

Figure 11. Mass spectrum of C_nLa cluster complexes and bare C_n clusters as observed by Heath et al.[7] when $LaCl_3$-doped graphite is laser vaporized (ArF 6.5 eV, 10 mJ cm^{-2}). Note the particularly strong peak for $C_{60}La$ and the absence of a peak for $C_{60}La_2$. This result is discussed in section VI (adapted from ref 7).

C_{60}^+ in a sooting flame. These observations are discussed in more detail in section VII.

V. Stability and Intrinsic Properties of C_{60}

After the buckminsterfullerene structure was proposed[3] the intrinsic properties of the species were probed by the Rice/Sussex group.[50-54] It was clearly vital to determine how reliable the experimental observation of the "stability" of the C_{60} cluster was, i.e. how "special" or "magic" the cluster actually was and how certain one could be about the buckminsterfullerene hollow cage explanation. After all, the proposal appeared to rest entirely on the observation of a single, strong mass spectrum peak at 720 amu (Figures 5 and 6), and such highly circumstantial evidence needed further support. Mass spectrometry is particularly susceptible to erroneous conclusions drawn on the basis of magic numbers due to the likely presence of ionization and fragmentation artifacts. Various aspects of the original experiment led to the conclusion that the cation mass spectrum (Figures 5 and 6) was most probably an accurate reflection of the neutral cluster distribution. Nevertheless it was necessary to carry out experiments in order to probe the behavior of C_{60} more deeply in order to generate further evidence, albeit still circumstantial, to support the stability conclusion and the cage structure proposal.

During the period from 1985 to 1990 many experiments were performed by a number of groups operating in the cluster field which probed carbon behavior with a view to confirming or falsifying the fullerene-60 proposal. If C_{60} really were a cage then the most obvious next step was to attempt to trap an atom inside the cage. The first result, in this context, was the observation of $C_{60}La$ by Heath et al.[7] By using a graphite disk, soaked in $LaCl_3$ solution a strong signal was obtained for the monolanthanum complex $C_{60}La$, with no evidence of a peak for $C_{60}La_2$ (Figure 11). Cox et al.[91] questioned the conclusion. They pointed out that, since C_{60} needs two 6.4 eV (ArF) photons for ionization and $C_{60}La$ only one, the relative strengths of the $C_{60}La^+$ and bare C_{60}^+ MS signals should not necessarily be taken as reliable gauges of their respective abundances, and a possible $C_{60}La_2^+$ signal might be too weak to detect

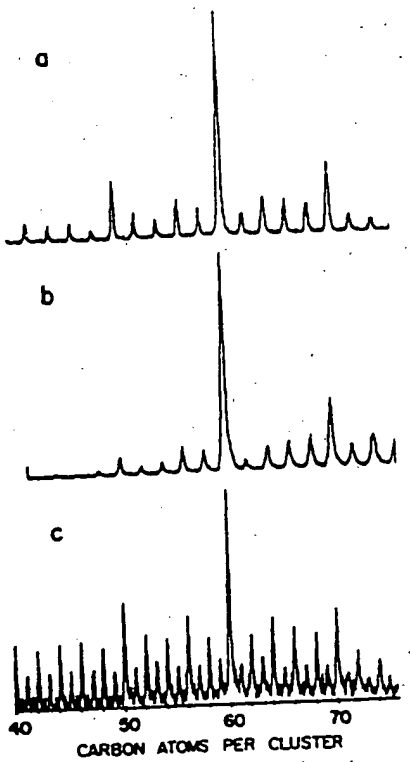

Figure 12. Carbon cluster ions observed under various production conditions.[52] (a) negative ions produced by directing a KrF excimer into the nozzle during expansion, (b) positive carbon cluster ions produced directly during vaporization in the nozzle without the aid of the KrF excimer laser, and (c) negative ions produced directly during vaporization in the nozzle, again without the aid of the KrF excimer laser but with longer residence time in the clustering region than in the case of the positive ions depicted in b (reprinted from ref 52; copyright 1987 Gordon and Breach Science Publishers, Inc.).

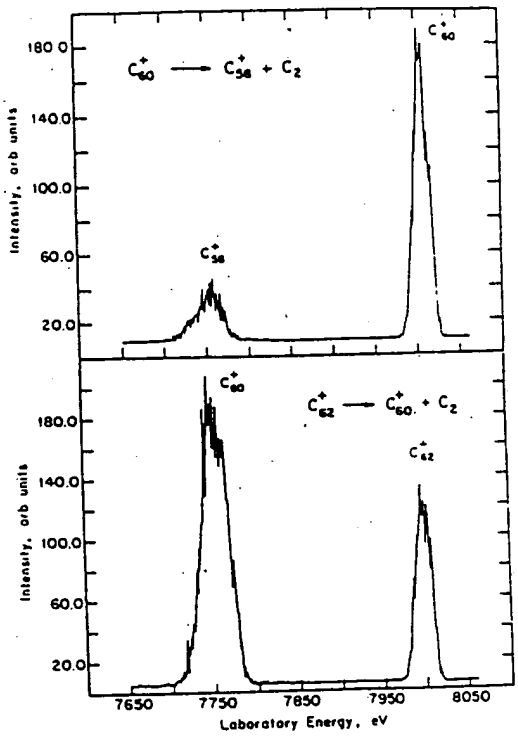

Figure 13. Metastable mass-analyzed ion kinetic energy scans (MIKES) published by Radi et al.[93] The parent ion (on the right) is mass selected by the magnetic analyzer and the horizontal axis is a scan of the electrostatic analyzer voltage. The parent ion energy is 8 keV. C_2 loss is observed from C_{60}^+ (above) and C_{62}^+ (below). Note the dramatic differences in metastable activity as reflected by the relative intensities of the product peaks, relative to their parent ions in these two cases (reprinted from ref 93; copyright 1990 the American Institute of Physics).

Cox et al.[67] have discussed further the cage hypothesis in general and metal atom encapsulation in particular and after detailed assessment they conclude that overall their observations are non-committal over whether C_{60} was a cage or not.

For the smaller carbon species the positive ions display the well known magic numbers: 11, 15, 19, 23 (the so-called "Δn = 4" effect, cf. Figure 4) whereas the negative ions exhibit a different sequence.[21-24,12] The paper announcing the original discovery[3] assumed that the mass spectra (Figures 5 and 6) reflected accurately neutral carbon cluster distributions. If the buckminsterfullerene structural proposal were correct however, the positive and negative ion distributions would be expected to exhibit a similar prominence for the 60-carbon atom analogue. The first experiment to probe this possibility[64] showed that negative ions, produced by laser ionization just after the cluster beam exited from the nozzle exhibited an anion mass spectrum in which C_{60}^- was dominant. In this experiment the neutral species became negatively charged by electron transfer. If the positive or negative ions, produced directly by vaporization are studied, it is found that only after clustering is allowed to continue for a significant length of time is the C_{60}^- anion dominant[66] otherwise it is not.[65] Some examples of mass spectra recorded under various conditions[51,64,66] are presented in Figure 12. Cox, Reichmann, and Kaldor[67] describe some intriguing relative time-of-flight differences in behavior between various individual clusters, in particular C_{28} and C_{60}, which are highly dependent on the nozzle parameters. These experiments appear to suggest that wall reactions may occur in the nucleation channel. It is possible that what was observed in this experiment was C_{60} deposited in the channel which subsequently desorbed. The main evidence for the importance of wall effects lies in the detection of $C_{60}K$ clusters when a new, pure (i.e. K free) carbon target replaces a previous one doped with potassium.

Important observations have had a bearing on the stability of C_{60}. The very early experiments by Bloomfield et al.[28] showed that C_{60} was susceptible to multiphoton fragmentation. A series of studies by Bowers and co-workers[92-94] showed that C_{60} could undergo metastable fragmentation. Particularly interesting is the observation that C_{60} exhibits much lower metastability than other neighboring clusters such as C_{58} as shown in Figure 13. These results suggest that hot C_{60} may exhibit phenomena associated with fluidity—perhaps an intriguing form of surface fluidity. On the

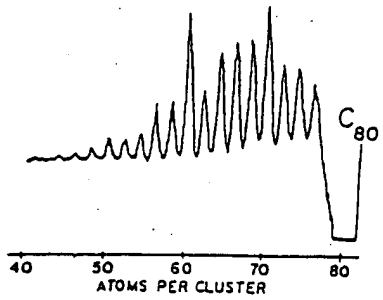

Figure 14. Fragmentation products under ArF (15 mJ cm^{-2}) irradiation observed by O'Brien et al.[95] Under irradiation the mass selected C_{60}^+ cluster (including ca. 20% C_{70} and ca. 10% C_{80}) is here seen to fragment into smaller even clusters: C_{70}, C_{70}, etc. by loss of C_2, C_4, etc. Particularly interesting is the observation that C_{60} and C_{70} are favored fragmentation products (reprinted from ref 95; copyright 1988 the American Institute of Physics).

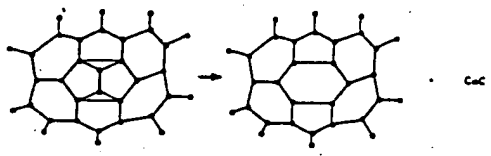

Figure 15. Hypothetical fragmentation–rearrangement mechanism presented by O'Brien et al.,[95] involving C_2 loss and cage re-sealing which could explain the fragmentation phenomena in Figure 14 (reprinted from ref 95; copyright 1988 the American Institute of Physics).

other hand, O'Brien et al.[95] and Weiss et al.[96] have shown that cold C_{60}^+ exhibits little, if any, evidence for fragmentation. The likely explanation for this disparity is that clusters produced under the vacuum vaporization conditions[28,92-94] possess massive amounts of internal energy leading to metastable C_{60}^+. As special behavior is most dramatic after extensive degrees of nucleation have occurred it is possible that the C_{60} signal observed under vacuum ablation conditions is actually a mixture of isomers, at least in part. Related studies by Hasselberger et al.[78] show that metastable fragmentation is less severe when clusters are produced with lower internal energies. The measurements of O'Brien et al.[95] showed that multiphoton fragmentation of clusters with 32–80 atoms occurred by elimination of even carbon fragments, C_n (n = 2, 4, 6, ...), rather than lower energy C_3 species. Particularly intriguing is the observation that large clusters, with 70 or more atoms fragment to form smaller even-cluster distributions in which C_{60} is special (Figure 14). Clusters with less than 32 atoms fragment into a range of smaller carbon species, a result interpreted as evidence that clusters with less than 32 atoms were not cages. O'Brien et al.[95] also presented an interesting mechanism for this process which is depicted in Figure 15. Laser irradiation studies by Weiss et al.[96] showed that the metal complexes were also quite resistant to photofragmentation. They also showed that multiphoton fragmentation of $C_{60}M^+$ resulted in metal-complex products C_nM^+ for which the critical smallest sizes occur at n = 48, 44, 44–42 for M = Cs, K, and La, respectively (Figure 16). This result provided strong circumstantial evidence for metal atom encapsulation because the minimum physical cage size scales with the ionic radius

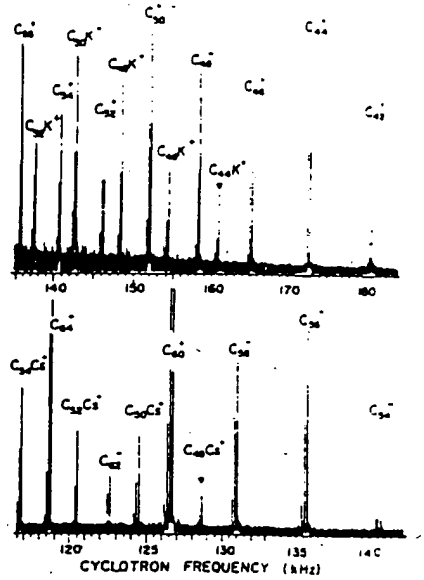

Figure 16. High-order photofragmentation pattern of $C_{60}K^+$ (above) and $C_{60}Cs^+$ (below) detected by FT-ICR mass spectrometry by Weiss et al.[96] The break-offs observed at $C_{48}Cs^+$ and $C_{44}K^+$ are in excellent agreement with expectation for the smallest fullerene networks capable of encapsulating the metals, based on the known ionic radii (reprinted from ref 96; copyright 1988 American Chemical Society).

of the metals in the series.

Prior to the isolation of macroscopic samples of the fullerenes (section IX) several experiments were carried out in order to determine their physical, mainly spectroscopic, properties. Tandem TOF-MS experiments were devised to explore the possibility that the spectra of C_{60} (neutral) and C_{60}^+ (the positive ion) might be responsible for the astrophysically intriguing diffuse interstellar bands (section XI). These experiments involved the resonant photodissociation of a van der Waals complex of benzene with neutral C_{60} and C_{60}^+. It proved possible to photofragment C_{60}-C_6H_6 but not the ion complex, C_{60}^+-C_6H_6, probably because charge transfer forces bind the adduct too tightly in the ion complex.[97] Very weak photofragmentation of the neutral complexes of C_{60} with C_6H_6 and CH_2Cl_2 was observed at 3860 Å by depletion spectroscopy.[98]

Yang et al.[99] used an ingenious technique developed by Cheshnovsky et al.[100] to observe the UV photoelectron spectra of negative cluster ions. In these experiments the spectra of carbon clusters from C_{48} to C_{84} have been observed. Of particular interest are the UPS patterns of C_{50}, C_{60}, and C_{70} which show a low energy LUMO feature consistent with closed shells for the neutral species. C_{60} had the lowest electron affinity: viz 2.6–2.8 eV. These obeervations provided further strong support for the fullerene proposal. The ionization potential of C_{60} was obtained in an elegant way by Zimmerman et al.[101,102] who used a series of charge transfer measurements with various reactants of known IP to bracket the IP of C_{60}: 7.61 ± 0.11 eV. This result was consistent with conclusions drawn from early experiments which indicated that the IP lay between the energy of the ArF excimer laser (6.4 eV) and that of the F_2 laser (7.9 eV) because C_{60} was 2-photon ionized by

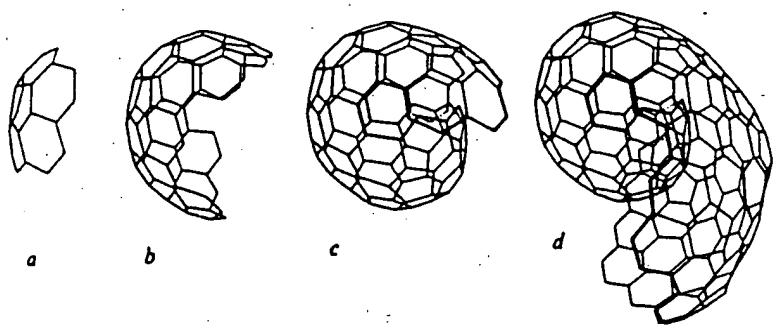

Figure 17. Diagramatic representation[108] of a hypothetical carbon vapor nucleation scheme[103,108] proposed for the formation of concentric shell graphite microparticles. Note that the structure c has overlapped and so trapped the trailing edge inside the spiraling network. This species is thus essentially the embryo for further growth. It is proposed that C_{60} might be produced by a modification of this process in which the edges meet and seal to form a closed cage. In such a case further growth by chemical bond formation might be expected to be halted. It was conjectured that similar structures might occur as intermediates during soot nucleation (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

ArF and 1-photon ionized by F_2.[103,67]

As mentioned in section IV, the most intriguing and convincing spectra were those obtained in the infrared study of Krätschmer, Fostiropoulos, and Huffman in 1990[5,74] (see further details in sections VIII and IX).

VI. Reaction Studies

The first reaction studies aimed at probing the cage concept were those of Heath et al.[7] and Cox et al.[91,67] (discussed in section V) who studied the carbon/metal complexes. Rohlfing et al.[25] and Heath et al.[29,30] carried out similar reaction studies which focused mainly on the properties of the carbon chains. It is also important to note that van der Waals complexes can form in the supersonic beam if C_{60} is cold.

When various gases such as CO, NO, and SO_2 were introduced into a reactor, placed downstream from the nozzle in which C_{60} is formed, Zhang et al.[103] showed that all the even carbon clusters were totally unreactive. The odd clusters were, on the other hand, very reactive. These experiments gained significant further support from the studies of McElvany et al.[70] and Weiss et al.[98] which showed C_{60} and its analogues to be extremely unreactive in an ICR trap. However if gases are mixed with the driver gas in the nozzle, reactions can take place before and after C_{60} is formed. With hydrogen, a wide range of hydrocarbon products is detected (Rohlfing,[104] Hallett et al.,[105] and Doverstal et al.[106]). Rohlfing has used an in-line reflectron modification of the cluster beam technique and made some very careful high-resolution mass spectrometric measurements of the reactions of clusters C_{20}–C_{80} with hydrogen.[104] The variations in reactivity appear to be structure related and consistent with the cage proposal. The study suggests that chain cluster species with as many as 44 carbon atoms may be present. Complementary experiments by Hallett et al.[105] and Doverstal et al.[106] indicate that clusters in the C_{20}–C_{40} range show at least three different types of reactivity as evidenced by the mass spectrometric patterns of the hydrogenated products. The observations[105] are consistent with the proposal that small fullerenes (C_{20}, C_{24}, C_{28}, C_{32}, C_{50}) can form.[6] They are also consistent with the fact that formation that no 22 atom fullerene can exist, as pointed out by Fowler and Steer.[107]

VII. Gas-Phase Carbon Nucleation and C_{60} Formation

It would appear that most workers in the field are able to observe special behavior fairly easily and under a wide range of conditions, all of which have one major feature in common: C_{60} appears to be dominant *only* when nucleation nears completion, leaving behind C_{60} and other even-numbered relatives such as C_{70}. This result has one obviously simple explanation; at least some fraction of the even clusters—particularly C_{60}—is unreactive toward growth into macroscopic particles. The spontaneous creation of C_{60} requires a mechanistic explanation. In particular, entropy factors clearly need to be carefully assessed when it is proposed that so symmetric an object is formed in a chaotic plasma. A feasible nucleation mechanism was provided by Zhang et al.[103] and refined further by Kroto and McKay.[108] The nucleation model proposes that curved sp^2-linked (aromatic) carbon networks form (Figure 17) and can serve as embryos for further growth. The energetics of sheet carbon cluster radicals is invoked to explain the curvature/partial closure. Essentially the drive toward closure is governed by the energy released as a result of eliminating the edge dangling bonds. For instance a flat graphite-like sheet of 60 atoms would have at least 20 dangling bonds, whereas fullerene-60 would, of course, have none. In general, in a chaotic system, partly closed, overlapped embryos, such as that shown in Figure 16c, are expected to form and which, once overlapped, cannot close perfectly. These species are probably highly active nucleation sites to which permanent chemical binding of adsorbing fragments can take place. Of course some form of closure/annealing process might take place if the temperature is high enough for intra and extra network rearrangement to occur. It was proposed[103,108] that during this general spiral nucleation process some embryos would close forming fullerenes, particularly fullerene-60 which would no longer present a site for efficient accretion. The process is primarily a physicochemical nucleation scheme in which the fullerenes act as deadends for the most rapid nucleation.

After embryo formation, epitaxial growth has been shown to result in icospiral graphitic giant molecules or microparticles[108] with structures consistent with

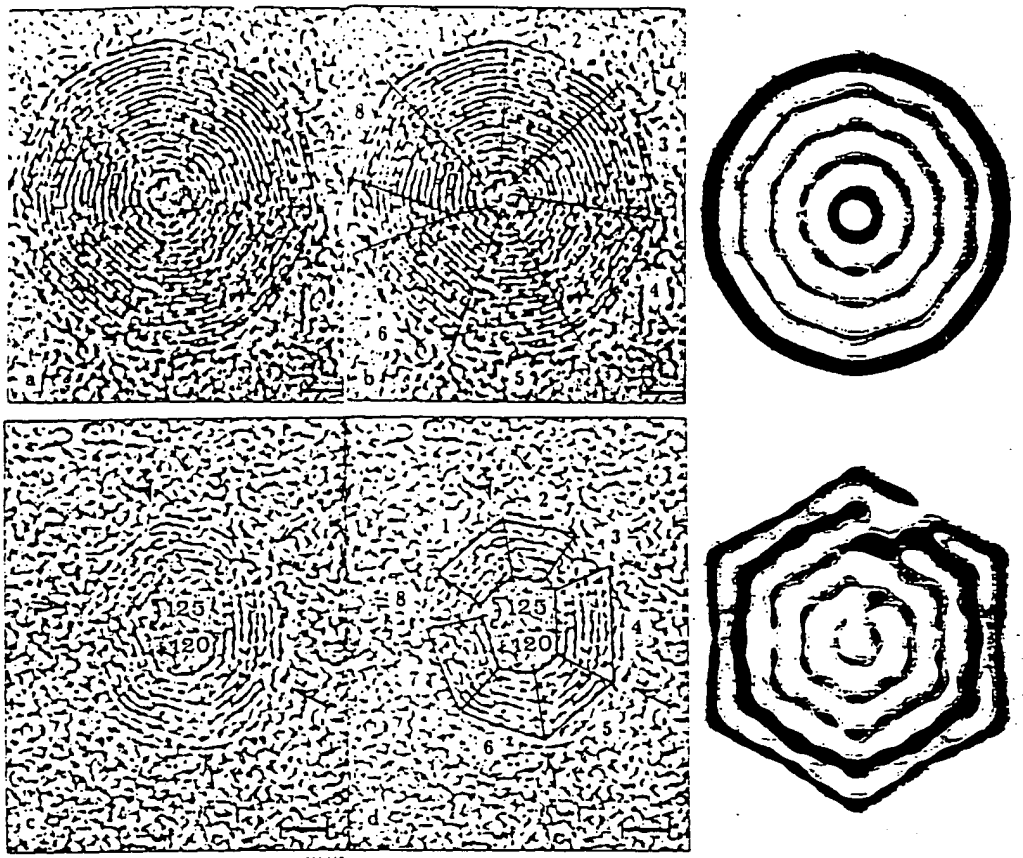

Figure 18. Comparison by McKay et al.[111,112] between TEM images of polyhedral graphitic microparticles observed by Iijima[109] and simulated TEM images for a hypothetical spiral shell particle predicted by the nucleation scheme depicted in Figure 17. The fairly round particle observed by Iijima which is depicted in a and b is seen to exhibit a similar pattern to the simulation top right. On the other hand the more polygonal particle, shown in c and d, exhibits a similar pattern to the simulation shown bottom right. The simulations are for the same particle observed from different angles. The hypothetical particle has shell interconnections which can most easily be seen in the lower right simulation. In b and d the polygonal outlines are delineated.

those of spheroidal graphitic microparticles observed by Iijima in 1980.[109,110] Kroto et al.[111,112] have provided further support for the scheme in the form of TEM image simulations based on the icospiral concentric shell structure concept,[108] in excellent agreement with the Iijima images as depicted in Figure 18. Roulston et al.[113] have shown that certain electronic and structural properties of amorphous semiconducting carbons can be explained on the basis of a spheroidal graphitic infrastructure, rather than by the traditional flat microstructure. Yacaman et al.[114,115] have shown that FT power-spectra processed, electron microscope images of carbon microparticles appear to be consistent with the quasiicosahedral spiral substructure.[108] Attention has been drawn to the fact that small graphitic microparticles actually consist of crystalline quasiicosahedral graphitic cores surrounded by amorphous carbon surface layers.[116,109] Interestingly, Iijima[110] has shown that the TEM structure at the nucleus of one of the carbon microparticles, studied earlier[108] was consistent with the image expected if it were a C_{60} cage. With hindsight this result demands further serious investigation to see whether fullerene-60 can itself be encapsulated during later stages of particle growth.

Wales[117] has considered some statistical aspects of the growth dynamics of closed-cage structures and Bernholc and Phillips have discussed the kinetic factors involved in the growth of carbon clusters in general.[118]

It was also suggested that a modified form of the nucleation scheme, devised to account for the spontaneous creation of C_{60}, could also explain the spheroidal nature of soot.[103,108,50,51,119] This proposal was criticized by Frenklach, Ebert, and co-workers[120-123] who favor an earlier theory, which invokes the physical condensation of flat PAH molecules held together by van der Waals forces into coagulating liquid drops. However, Harris and Weiner point out how little has been firmly established about the soot formation mechanism.[124] It can in fact be demonstrated[125] that the new scheme is broadly consistent with kinetic, structural, and chemical observations made on soot and its formation process.

The new nucleation scheme predicts that some C_{60} should form as a byproduct[103,108] of soot production. Subsequently Gerhardt, Löffler and Homann,[87-90] in studies of the ions produced in a sooting flame, found conditions under which the mass spectrum shown in

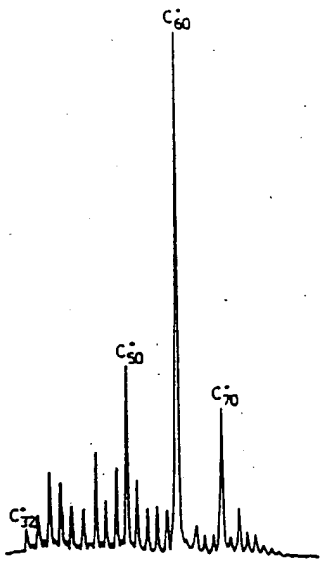

Figure 19. Mass spectrum, observed by Gerhardt, Löffler, and Homann,[87-90] of positive ions produced by a sooting benzene–oxygen flame (C/O = 0.76) (reprinted from ref 87; copyright 1987 Elsevier Science Publishers).

Figure 19 is obtained. This spectrum is almost identical with that observed during the pure carbon laser vaporization experiments where C_{60}^+ is the dominant ion! Homann and co-workers conclude that this observation should not be taken as support for the new spiral nucleation scenario as the tell-tale even ions with a dominant C_{60}^+ peak are not seen until after the inception of soot particle formation. The carbon/hydrogen reaction studies[104-106] promise to shed further light on the soot formation process, but the way in which the results might dovetail with the conventional data remains to be ascertained. Kroto has summarized the present state of affairs from this viewpoint.[125]

VIII. Theoretical Studies of the Fullerenes

Theoretical studies predating the discovery of C_{60} have been discussed in section II. After the discovery, theoreticians had a ball and many aspects of the molecule's properties have already been probed. The comprehensive overview of theoretical work on fullerene-60 presented by Weltner and Van Zee[2] is here conflated with more recent work.

One important aspect of the original experimental observations was the fact that C_{70} *also* showed special behavior. Topological and chemical stability arguments, as discussed by Kroto[8] and Schmalz et al.,[7] explain this observation as being entirely consistent with the fullerene proposal. Indeed these studies suggested that if the C_{60} mass spectrometric signal were due to its having a closed cage fullerene structure, C_{70} should show special behavior also, for the same reason. Thus, most importantly and rather convincingly, the fullerene structure proposal no longer rested on the single line observation. In fact it had now gained significant further support by the fact that a prediction had been made and neatly confirmed. Indeed the two observations, taken together, provided convincing evidence for the existence of a whole family of fullerenes and further probing suggested that in addition to C_{60} and C_{70}, the C_{24}, C_{28}, C_{32}, and C_{50} clusters (Figure 20) should also show varying degrees of special stability[8,9] (N.B. fullerene-22 cannot exist[107]).

The dominance of C_{60} and C_{70} was ascribed to the fact that these are the smallest fullerenes that can have an isomer (one in each case) in which none of the 12 pentagonal configurations, necessary and sufficient for closure, abut.[8,9] It was shown[8,50] that the predictions were commensurate with the mass spectrum obtained by Cox et al.[67] (Figure 21) and consequently there existed convincing experimental evidence for the fullerene *family* proposal. Since even-numbered carbon clusters are detectable with as many as 600 or more carbon atoms,[84] the possibility of giant fullerenes[108,126] such as C_{240} and C_{540} shown in Figure 22 appears to be an exciting possibility.[60]

Isomer stability has been discussed by Stone and Wales[127] who noted that the difference in energy between isomers is small and suggested that the C_{60} signal should be due to a mixture of isomers. This result is difficult to reconcile with the observation (Figures 5 and 6) since it leads to the conclusion that C_{60} is no more special than other clusters such as C_{62}. Potential energy functions have now been developed for the carbon cages systems by Takai et al.[128] and Balm et al.[129] The simulated annealing, Monte-Carlo methods used by Zerbetto[130] to study the behavior of small carbon clusters have been applied by Ballone and Milani[131] in order to show that the fullerene cages are minimum energy structures.

A group theoretical analysis of the electronic properties of the fullerene family, by Fowler and Steer,[107] showed that the members, C_n where $n = 60 + 6k$ (k = 0, 2, 3, 4, ..., i.e. an integer other than one), should have closed-shell electronic structures. The degree of aromaticity in a compound is of interest, and the number of Kekulé structures is often considered to be a guide. A total of 12 500 for fullerene-60 has been calculated

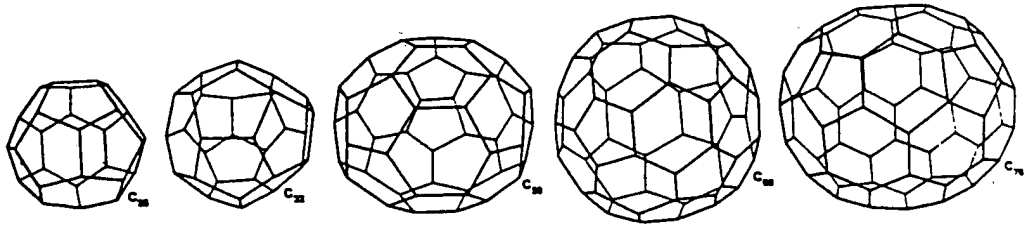

Figure 20. Five possible "magic" fullerenes predicted to display enhanced stability, relative to others in the range with 20–80 atoms, on the basis of chemical and geodesic factors[8] (reprinted from ref 8; copyright 1987 Macmillan Magazines Ltd.).

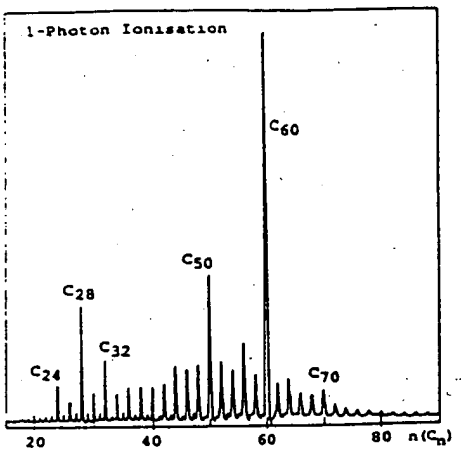

Figure 21. Time-of-flight mass spectrum taken from the data of Cox, Reichmann, and Kaldor.[67] The strong peaks are in excellent agreement with expectation[6,9] if they correspond to fullerenes. The fullerenes 24, 28, 32, 50, 60, and 70 (Figure 20) are predicted to exhibit enhanced stability, i.e. are magic. Note the sharp cutoff at C_{24} which is consistent with the fact that a no 22 atom fullerene can form.

by Schmalz et al.,[132] Hosoya,[133] Brendsdal and Cyvin,[134] and by Elser.[135] Resonance circuit theory has been applied to this problem by Schmalz et al.,[132,9] Klein et al.,[136,137] as well as Randic, Nikolic, and Trinajstic.[138-140] These studies indicate that account must be taken of the fact that some resonance structures make negative contributions to the aromatic stabilization. Schmalz et al.[9] compared resonance circuit theory with Hückel molecular orbital (HMO) theory and concluded that C_{60} should be less aromatic than benzene. Amic and Trinajstic[140] discuss stabilization arising from bond delocalization. Graph theory has been applied to C_{60} and to other systems by Balasubramanian and Liu[141,142] and also by Dias who has circumvented group theory in order to simplify Hückel calculations.[143] Hückel calculations on fullerene-60 have been made by Haymet[144,20] and the stabilization due to delocalization discussed. Jiang and Zhang[145] have calculated the stability of fullerene-60 by Hückel theory using moment analysis techniques. Hess and Schaad[146] as well as Aihara and Hosoya[147] have also applied Hückel theory to the problem, focusing on aspects of spheroidal aromaticity.

Fowler and Woolrich[148] have made three-dimensional HMO calculations which predict that C_{60} and C_{70} are closed shell systems. Fowler[149] extended this approach in order to assess the stability in other, larger fullerene cages, while Fowler, Cremona, and Steer[150] have discussed bonding in nonicosahedral spheroidal fullerene cages. Fowler[151] has extended these ideas to various classes of cylindrical fullerenes and predicted closed electronic shells with an empty nonbonding orbital for clusters consisting of $10(7 + 3k)$ and $12(7 + 3k)$ atoms with 5- and 6-fold symmetry. Ceulemans and Fowler[152,153] considered possible Jahn–Teller distortion pathways for icosahedral molecules.

Byers Brown[154] has discussed the simplification that high symmetry imparts to π-system calculations and obtained algebraic solutions for the orbital energies of fullerene-60. Electronic and vibrational properties were calculated by using a two-dimensional HMO method by Coulombeau and Rassat.[155] Semiempirical calculations including the effects of nonplanar π-orbital overlap due to curvature have also been carried out by using the free-electron model in the Coulson–Golubiewski, self-consistent Hückel approximation by Ozaki and Takahashi.[156] Haddon et al.[157,158] have also considered the effects of nonplanarity, i.e. pyramidalization.

Extended Hückel calculations by Bochvar, Gal'pern, and Stankevich[159] and INDO and INDO/CI calculations by Feng et al.[160] have been applied to C_{60} and its isomers. A comparison between C_{60} and graphite was made by MNDO with geometry optimization by Newton and Stanton.[161] McKee and Herndon[162] also applied MNDO theory to cage carbons and concluded that the flat "graphitene" cage,[144] in which two coronene sheets are linked by pentagonal rings at the edge to form a disk-like structure should be more stable than fullerene-60. These authors also considered the mechanism of formation arising from rearrangement. Rehybridization and bonding were studied by Haddon, Brus, and Raghavachari who applied the π-orbital axis vector/3d-HMO (POAV/3D HMO) method[157,158] and concluded that larger clusters were favored. It was also postulated that fullerene-240 should be more stable than C_{60}. Lüthi and Almlöf[163-165] have carried out

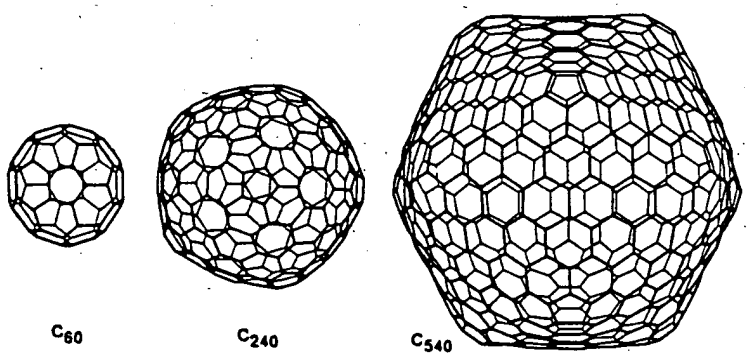

Figure 22. The set of fullerenes C_{60}, C_{240}, and C_{540} with diameters in the ratio 1:2:3. Kroto and McKay[108] showed that quasiicosahedral shape develops rapidly for the giant fullerenes. Strain in the giant fullerenes is expected to be focused in the regions of the corannulene-like cusps. The surface thus becomes a smoothly curving network connecting the twelve cusps (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

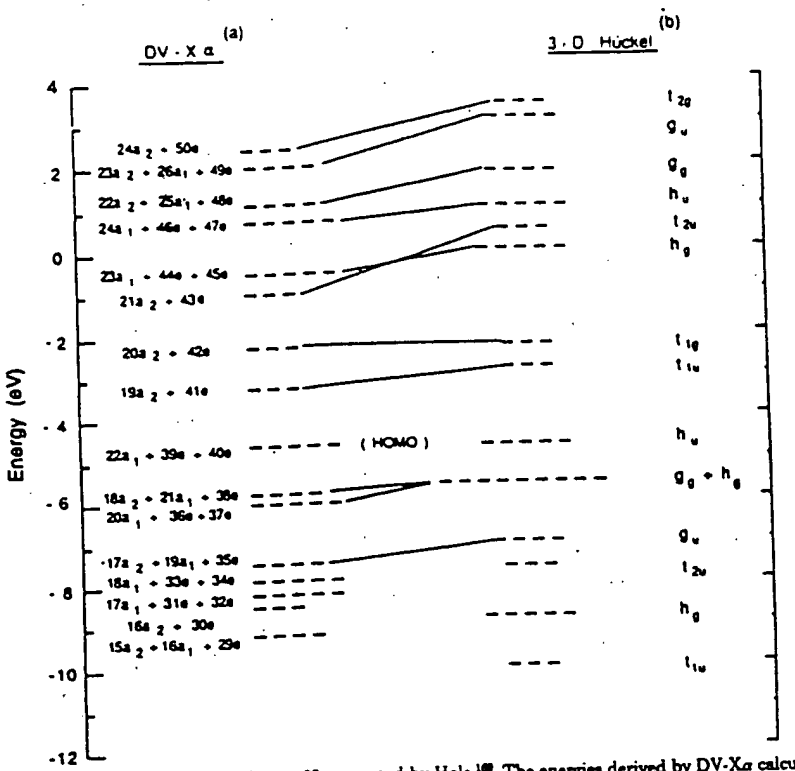

Figure 23. Orbital energy level diagram for fullerene-60 presented by Hale.[169] The energies derived by DV-Xα calculations assuming D_3 symmetry on the left are compared with Hückel results. In the diagram β has been given the value −2.52 eV (reprinted from ref 169; copyright 1986 American Chemical Society).

large-scale restricted Hartree-Fock calculations and they deduced that ΔH_f = 415–490 kcal/mol (relative to graphite) the electron affinity should be 0.8 eV and the ionization energy 7.92 eV. The electron affinity (2.4 eV) has been calculated by Larsson, Volosov, and Rosen[166] and by Braga et al.[167] Schulman and Disch[168] have calculated the heat of formation on the basis of ab initio SCF theory.

Hale[169] determined electronic properties, such as the ionization energy for fullerene-60, by the discrete variational (DV)-Xα method using the Slater transition state formalism. Such calculations tend to be good for spheroidal systems. Hale's orbital energy level diagram for fullerene-60 is reproduced in Figure 23. The linear combination of muffin-tin orbital method in its atomic sphere approximation (LMTO ASA) was applied by Satpathy.[170] Calculations in which the partial retention of differential overlap PRDDO approach was applied were carried out by Marynick and Estreicher.[171] Stone's tensor surface harmonic theory was used by Fowler and Woolrich.[148] The IMOA method (iterative maximum overlap approximation) was applied to a range of fullerenes by Kovacević, Graovac, and Babić[172] to assess hybridization, structure and the amount of strain in these cages. Haddon[173] has discussed degree of pyramidalization considerations for fullerene-60 and other aromatic compounds.

Fabre and Rassat have reviewed the properties of known aromatic molecules which are essentially com-

In some of the calculations the electronic spectra of the fullerenes were the main focus. The calculations of Kataoka and Nakajima[175] and Lászlō and Udvardi[176] used the Pariser–Parr–Pople method (with CI) to determine spectra, structural parameters, and oscillator strengths. Optimized INDO calculations were published by Shibuya and Yoshitani.[177] The electronic structure and the spectra have also been studied by the CNDO/S method (including CI) by Larsson et al.[166] and by Braga et al.[167] Hayden and Mele[178] evaluated π-bonding behavior using the tight-binding model with electron–phonon coupling for the ground and excited states of fullerene-60. Jahn–Teller instabilities in the excited electronic states and the ion have been classified by Negri, Orlandi, and Zerbetto[179] who have also estimated Franck–Condon patterns and phosphorescence quantum yields.

Several calculations focused on the vibrational properties of fullerene-60. The result of primary (and historical) significance is that only four fundamentals are IR active due to the high symmetry of the molecule. Of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, four have t_{1u} symmetry and are IR active whereas 10 (eight h_g and two a_g) are Raman active.

Newton and Stanton[181] gave preliminary details of the vibrational behavior of fullerene-60 using MNDO theory. A non-Cartesian coordinate method was employed to describe the C_{60} vibrations in terms of four-force field constants by Weiss, Jalaki, and Cooper.[180] Ab initio

SCF/STO-3G calculations of the vibrational properties of C_{60} and other symmetric carbon cages have been published by Disch and Schulman.[181] Schulman et al.[182] have applied the ab initio and AM1 methods to fullerene-24 and fullerene-60 in order to obtain heats of formation, vibrational frequencies, and ionization energies. Coulombeau and Rassat have considered the vibrations of several fullerenes up to fullerene-120.[183] They have also discussed hydrofullerenes.[184] In addition to calculating the rotational properties on the basis of icosahedral symmetry analysis,[184] Weeks and Harter have carried out a normal mode study on the basis of a classical spring/mass model.[185] They have also discussed the rovibrational properties of fullerene-60.[185-189] Stanton and Newton[190] extended and revised earlier MNDO studies giving detailed information on the normal modes. They have derived group theory invariance theorems for vibrational analysis and have discussed the A_u vibration which essentially consists of rotary oscillations of the pentagonal rings. Cyvin et al.[191] used a 5-parameter force field to calculate the frequencies of the four IR active and 10 Raman-active modes; and Brendsdal et al.[192] have considered approximate methods in order to determine all 46 vibrational frequencies. Brendsdal[193] has discussed the symmetry coordinates.

Slanina et al. have carried out a harmonic vibrational analysis within the AM1 method for fullerene-60 and also fullerene-70.[194] The study has been extended to include consideration of structural, energetic, and thermodynamic properties of both species using MMP2 and MNDO methods.[195-197] Bakowies and Thiel[198,199] have used the MNDO approach to calculate the IR spectra of a whole range of fullerenes from C_{24}–C_{240}. For C_{70} they deduce that one vibrational band should be significantly more intense than the rest, see section X.

Heymann has discussed the possibility that He may be trapped in a fullerene-60 cage.[200] Calculations have been made of the spectroscopic properties of various intracage complexes by Ballester et al.[201] assuming the central atom is trapped in a polarizable uniform (spherical) dielectric cage. Kroto and Jura[202] have discussed the importance of charge-transfer processes in the spectra of neutral and ionic fullerene intra- as well as extracage (van der Waals) complexes. For the ions the energy is just the difference between the ionization potentials of the C_{60} cage and the encapsulated species. Van der Waals complexes such as $C_{60}{\cdot}H^+$ are likely to be particularly important (section XI). Rosen and Waestberg have calculated the electronic structure of $C_{60}La$ (and C_{60}) obtaining ionization energies and electron affinities for the neutral and ionic species within the local-density approximation.[203,204] Saito[205] has also used the local density approximation to calculate the electronic properties of $C_{60}M$ (M = K, O, Cl).

Theoretical calculations have been carried out on fullerene-60 derivatives such as hydrofullerenes by Coulombeau and Rassat[184] and by Scuseria[208] who has also considered the perfluorofullerene, $C_{60}F_{60}$. Crystal packing considerations for spheroidal molecules including fullerene-60, have been discussed by Williams.[207]

Several papers have focused on the likely electrical and/or magnetic properties of the fullerenes in particular fullerene-60. Elser and Haddon[208,209] using HMO

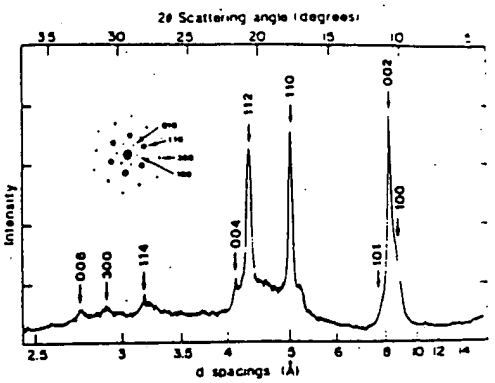

Figure 24. X-ray diffraction pattern of a microcrystalline powder of fullerene-60 obtained by Krätschmer, Lamb, Fostiropoulos, and Huffman.[4] Inset (upper left) is a single-crystal electron diffraction pattern (shown in more detail in Figure 25) indexed with Miller indices compatible with the X-ray pattern. This pattern provided unequivocal evidence that the C_{60} species they had isolated was a round ball 10 Å in diameter in perfect agreement with expectation for buckminsterfullerene (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

and London theory, calculated the ring current magnetic susceptibility and concluded that the shielding should be vanishingly small (less than 1 ppm) due to cancellation of the diamagnetic and paramagnetic contributions. They concluded that fullerene-60 should not show normal aromatic behavior. Studies by Fowler, Lazzeretti, and Zanasi[210] and Pauling[211] have suggested however that the diamagnetic term has been underestimated. From large scale ab initio, coupled Hartree–Fock calculations (involving all electrons) of the polarizability and magnetizability of C_{60} and C_{20}^{2+}, Fowler et al.[210] conclude that the shielding should be roughly the same as for related aromatic systems. Haddon and Elser[212] have discussed their own results[208,209] and reinterpreted those of Fowler et al.[210] and conclude that the latter study is consistent with a small delocalized susceptibility. Schmalz[213] has argued that the Fowler et al.[210] interpretation is correct. The NMR study of Taylor et al.[6] yielded a chemical shift for fullerene-60 which is fairly typical for an aromatic species. Fowler et al.[214] have extended their approach to the calculation of the shifts in fullerene-70, obtaining results consistent with observation and confirming the line assignments made by Taylor et al.[6] This problem is further discussed in section X.

IX. The Isolation, Separation, and Structural Characterization of Fullerenes-60 and -70

Almost five years, to the day, since the special behavior of the C_{60} signal was recognized (Figure 5) and the buckminsterfullerene proposal made,[3] macroscopic samples were isolated and characterized. Krätschmer, Lamb, Fostiropoulos, and Huffman,[4] in following up their earlier IR observations,[5,74] discovered that at ca. 300–400 °C a solid material could be sublimed from the deposit obtained from arc-processed graphite. They found that this sublimate was soluble in benzene and could be crystallized. The X-ray and electron diffraction analyses (Figures 24 and 25) of the crystalline material so obtained (Figure 26) showed it consisted of

Figure 25. Single-crystal electron diffraction pattern of fullerene-60.[4] Further details of indices are given in Figure 24 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

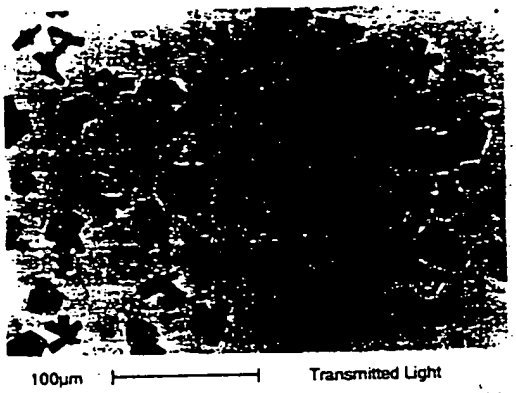

Figure 26. Transmission micrograph of crystals extracted by Krätschmer et al.[4] from the deposit of arc-processed graphite. Thin plateleta, rods and stars of hexagonal symmetry are observed (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

by ca. 3.1 Å (in graphite the interlayer distance is 3.4–3.5 Å). These authors also reported IR (Figure 27), UV/vis, and mass spectra of the extracted material. Bands of C_{70} were present (weakly) in the IR spectrum and, in the UV/vis spectrum, some features of fullerene-60 were masked by those of fullerene-70. These results provided the first confirmation of the fullerene-60 structural proposal.

In a parallel and independent study of similarly arc-processed carbon, Taylor et al.[6] had also shown that C_{60} was present by FAB-sampled mass spectrometry and that a red soluble extract could be obtained by treating the carbon deposit directly with benzene. Taylor et al.[6] processed the extract by the Soxhlet procedure and obtained a material which mass spectrometry showed to contain a range of fullerenes, C_{60} and C_{70} in particular (Figure 28). This material was chromatographed by using hexane/alumina, and C_{60} and C_{70} were thereby separated into a magenta and red fractions, respectively. ^{13}C NMR measurements yielded a single line for C_{60} (Figure 29a), providing definitive

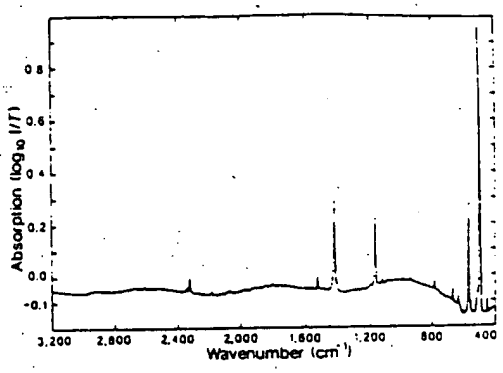

Figure 27. Infrared spectrum of fullerene-60 presented by Krätschmer et al.[4] showing the four fundamentals in excellent agreement with expectation for the proposed fullerene-60 structure. Weaker features belong to fullerene-70 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

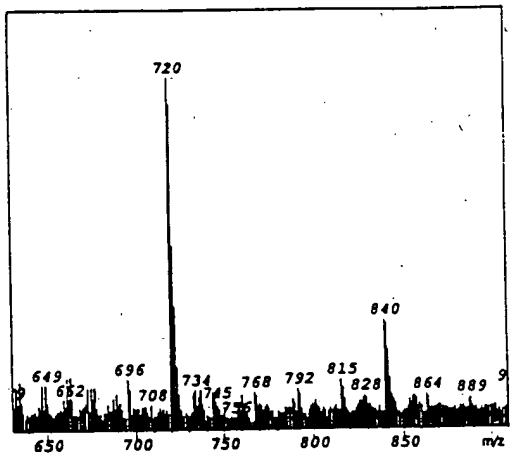

Figure 28. FAB-sampled mass spectrum, obtained by Taylor et al.,[6] of the soluble material extracted from arc-processed graphite. Apart from unequivocal evidence for C_{60} and C_{70} in the extract there is also evidence for other even-numbered carbon species, particularly C_{58} and C_{68} (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

proof that all 60 atoms are equivalent—a result totally commensurate with the buckminsterfullerene structure. There is of course the alternative solution that all the atoms are located on the perimeter of a monocyclic ring. This (explosively) unlikely possibility was eliminated by the NMR spectrum of C_{70} which consisted of a set of five lines (Figure 29c) with a chemical shift pattern and relative intensities commensurate with the fullerene-70 structure (Figure 30b) first suggested by Heath et al.[7] This result not only confirmed the fullerene 5/6-ring geodesic topology but also eliminated the possibility that the carbon atoms might be fluxional. Almost as important is the confirmation, by this result, of the existence of other members of the fullerene family.

X. Postbuckminsterfullerene Research—The First Results

Since the revelation that macroscopic samples of the fullerenes can be isolated and that they are soluble and

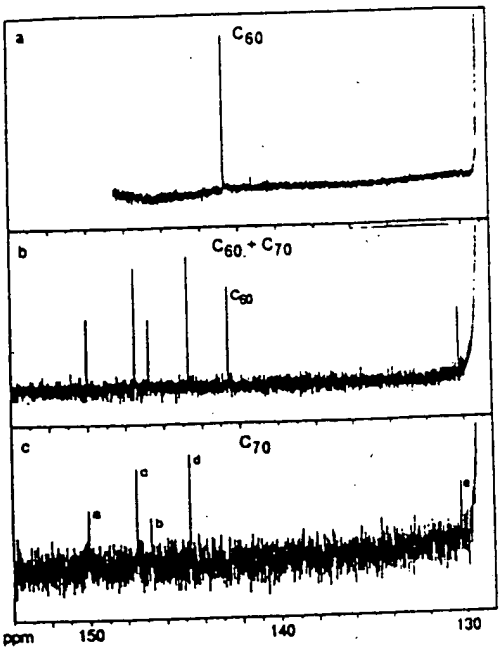

Figure 29. ^{13}C NMR spectra obtained from chromatographically purified samples (Taylor et al.[6]) of soluble material extracted from arc-processed graphite: (a) ^{13}C NMR spectrum of a purified sample exhibiting only a single resonance, (b) spectrum of a mixed sample, and (c) spectrum of a purified sample of C_{70} from which C_{60} has been eliminated. These spectra are consistent with the structures and assignments presented in Figure 20. The wing of the intense benzene solvent signal lies to the far right-hand side. This set of observations provided unequivocal evidence that the carbon atoms in C_{60} were indeed all equivalent in perfect agreement with expectation if the molecule were buckminsterfullerene (Figure 30). The five-line spectrum for C_{70} is also totally consistent with that expected for (D_{5h})fullerene-70 (Figure 30).[7] This spectrum eliminated any lingering doubt there might have been that the C atoms were either fluxional or perhaps located on the perimeter of a monocyclic ring. It also provided evidence for the stability of other members of fullerene family[7-9] (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

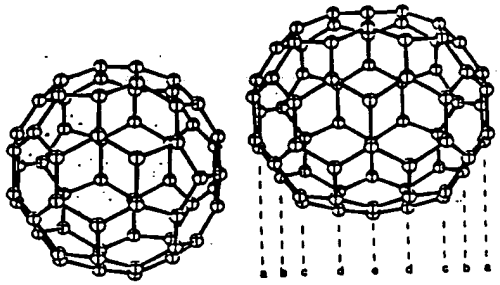

Figure 30. Schematic diagrams of fullerene-60 and fullerene-70 (based on diagrams of Slanina et al.[124]). All sixty atoms in fullerene-60 are equivalent whereas fullerene-70 possesses five different types of carbon in the ratios 10:10:20:20:10 in the order a:b:c:d:e respectively as shown. Compare with the NMR spectrum shown in Figure 29.

chromatographically separable, it is now the turn of experimentalist to have a ball. Ajie et al.[215] and Hare et al.[216] have observed the UV/visible spectra of chro-

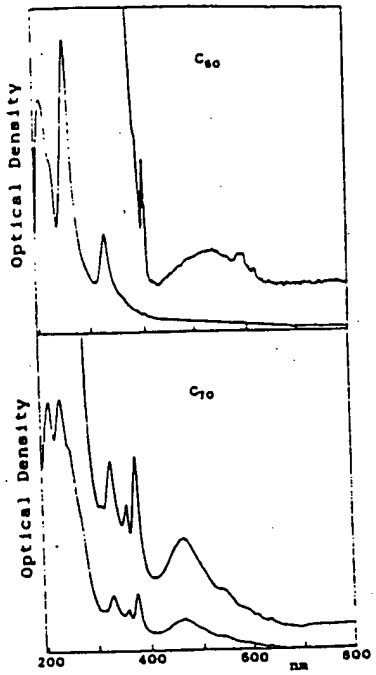

Figure 31. UV/vis spectra of chromatographically separated fullerene-60 and fullerene-70[215] in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

TABLE I. Properties of C_{60} Buckminsterfullerene

Vibrational Frequencies		
abs(obs)[a]	em(obs)[b]	calc, cm^{-1} [c]
528	527.1	472
577	570.3	618
1183	1169.1	1119
1429	1406.9	1434

X-ray Data[d,e]
r(C–C) = 1.388 (9) Å six–six ring fusion
r(C–C) = 1.432 (5) Å five–six ring fusion

NMR Data[f,g]
chemical shift (benzene soln) 142.68 ppm

Electronic/Spectroscopic Data	
electron affinity[h]	2.6–2.8 eV
ionization energy[i]	7.61 (0.02) eV
UV/vis bands[j,k]	213, 257, 329 (ϵ_{max} = 135 000, 175 000, 51 000) 404 (w) 440–670 (brd) (max. 500, 540, 570, 600, 625) nm

[a] Reference 4. [b] Reference 218. [c] Reference 191. [d] Reference 222. [e] See also Figures 24, 32, and 34. [f] See Figure 28. [g] Reference 6 (see also refs 215 and 228). [h] Reference 99. [i] References 101, 102, 239, and 240. [j] Reference 216 (see also ref 215). [k] See also Figure 31.

31). Reber et al.[217] have observed a luminescence spectrum. Frum et al.[218] have observed a most interesting IR emission spectrum from a hot gas-phase fullerene sample. The frequencies of the observed bands are given in Table I.

The availability of significant quantities of fullerenes has also opened up a Round Postbuckminsterfullerene Era of polycyclic aromatic chemistry. Haufler et al.[219] found that C_{60} can undergo Birch reduction to produce a white solid of formula $C_{60}H_{36}$. They point out that this formula is inconsistent with a pure hydrocarbon in

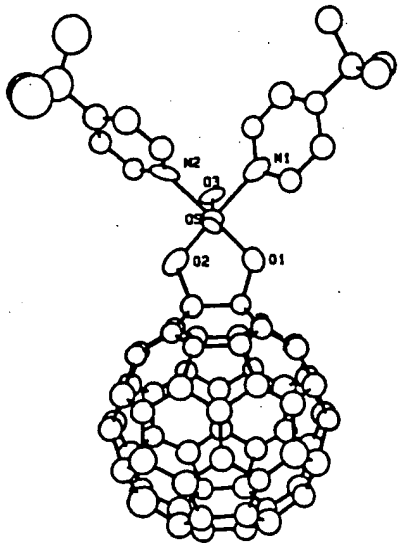

Figure 32. ORTEP drawing (50% ellipsoids) of the one-to-one C_{60}–osmium tetroxide adduct $C_{60}(OsO_4)$(4-*tert*-butylpyridine)$_2$ showing the relationship of the osmyl unit with the fullerene-60 carbon network[223] (reprinted from ref 222; copyright 1991 the American Association for the Advancement of Science).

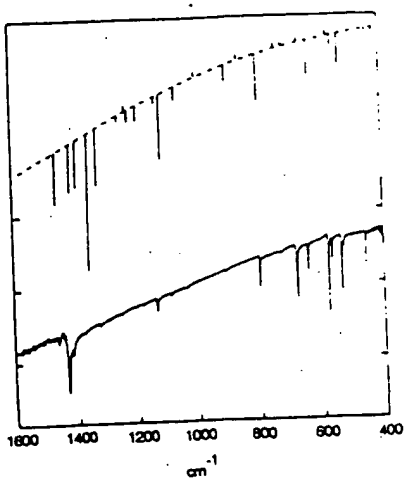

Figure 33. Infrared spectrum of chromatographically purified fullerene-70 obtained by Hare et al.[224] and compared with the calculated spectrum of Bakowies and Thiel.[198,199] The dashed curve is an estimated baseline. Note that the intensity of the very strong band calculated to lie near 1400 cm^{-1} has been arbitrarily reduced by a factor of 3 relative to other features. Features calculated to be very weak are indicated by markers *above* the estimated baseline (reprinted from ref 224; copyright 1991 The Royal Society of Chemistry).

which 12 isolated double bonds remain, possibly in the pentagonal rings. The reduction appears to be reversible. Evidence for the existence of a $C_{60}U$ complex was obtained by the laser vaporization approach, used originally to detect $C_{60}La$.[7] These authors also described the results of cyclic voltammetry measurements which indicated that C_{60} has two reduction potentials. Similar measurements have been made by Allemand et al.[220] who obtained a third potential. Their cyclic voltammetry measurements indicate that, curiously, fullerenes-60 and -70 appear to exhibit similar electrochemical behavior.

In one of the first attempts to introduce functional groups, Hawkins et al.[221] have found that they can form adducts of fullerene-60 with OsO_4(4-*tert*-butylpyridine) and its analogues. In a further study Hawkins et al.[222] have now obtained crystals of the osmium complex shown in Figure 32 and shown by X-ray analysis that rotation of the free C_{60} spheroids in the solid phase has been eliminated by the attached group. This study has yielded the first carbon–carbon bond lengths for the fullerene cage (Table I). Arbogast et al.[223] have observed fascinating photophysical behavior: fullerene-60 shows no fluorescence and efficiently catalyzes the formation of singlet oxygen. These authors observe a small S–T splitting of ca. 9 kcal/mol which is probably due to the large diameter of the molecule and the resulting small electron–electron repulsion energy. This together with the very low fluorescence rate and probably large spin–orbit interaction appears to account for the fact that intersystem crossing is a dominant process. Attention has been drawn to the fact that, due to their photophysical activity, care should be taken when working with fullerenes.

Hare et al.[224] and Bethune et al.[225] have made infrared measurements on chromatographically separated samples of fullerene-70 together with the calculated spectrum of Bakowies and Thiel[198,199] is presented in Figure 33. Bethune et al.[226] and Dennis et al.[227] have also made Raman measurements of fullerene-60 and -70. Liquid-phase NMR studies of unpurified fullerene mixtures by Johnson et al.[228] confirmed the result of Taylor et al.[6] (carried out on fully chromatographically purified samples) that the fullerene-60 resonance is a single line. Ajie et al.[215] have also confirmed the NMR measurements of a single line for fullerene-60 and five lines for fullerene-70; the former on a separated sample, the latter on a mixed fullerene-60/-70 sample. A 2D NMR analysis on fullerene-70 by Johnson et al.[229] has unequivocally confirmed the assignments made previously by Taylor et al.[6] shown in Figures 29c and 30b. Further refinements by Fowler et al.[214] of previous studies[210] predict fullerene-60 chemical shifts in excellent agreement with experiment (within 3 ppm). The study also includes estimates of the shifts for fullerene-70 so supporting further the pattern of line assignments given by Taylor et al.[6] (Figures 29c and 30b). Tycko et al.[230] and Yannoni et al.[231] have made solid-state NMR measurements down to 177 K where the motion is sufficiently slow for chemical shift tensor data to be obtained. Fullerene-60 rotates isotropically at 296 K and fullerene-70 rotates somewhat more anisotropically. Haddon et al.[232] have measured the magnetic susceptibility of solid samples of fullerenes and found it consistent with a molecule with a small ring current (see discussion in section VIII). Fowler[233] notes that when this result is compared and contrasted with the NMR shift of fullerene-60[6] it may imply ambivalent character when the question of the molecules "aromaticity" is considered.

Perhaps scanning tunneling microscopy (STM) offers more than any other a satisfying feeling of what the

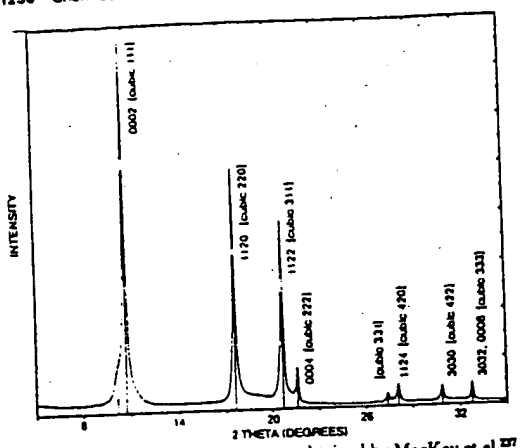

Figure 34. X-ray diffraction pattern obtained by MacKay et al.[227] from a chromatographically purified fullerene-60 sample. The structure revealed is basically that of a strongly disordered stacking of a simple hexagonal close-packing, exactly as for elemental cobalt. The hexagonal unit cell refines to $a = 10.017 \pm 0.004$ Å and $c = 16.402 \pm 0.01$, and contains two C_{60} spheres. The spheres would be 10.017 Å between centers and the calculated density would be 1.68 g cm^{-3}. The lines can be indexed as shown and it will be noted that, because of the stacking disorder, only those reciprocal lattice rows parallel to c for which $-h + k = 3n$ are present. The c/a ratio of 1.637 is very close to the theoretical value of 1.633 and thus the pattern can also be indexed with respect to a face-centered cubic lattice (with $a = 14.186$ Å) (as of copper metal) with stacking disorder which removes the 200 and 400 reflections and which introduces a very weak line (the first) at a spacing of $a/(8/3)^{1/2}$ due to double diffraction from stacking faults. The intensity variation of the pattern as a whole corresponds to the transform of a sphere of radius 3.5 Å giving a first minimum in the region of $2\theta = 25°$. Since the crystal is a mixture of FCC and HCP arrays, extracted crystalline material probably contains solvent molecules trapped in the faults.

et al.,[235] and Chen et al.[236] have deposited fullerene monolayers on gold and studied them by STM. The spherical molecules tend to form mobile hexagonally packed arrays on a surface. Chen et al.[236] observed local density variations on the surface of fullerene-60 which are highly suggestive of five- and six-membered rings.

The preliminary X-ray observations were made by Krätschmer et al.[4] working with crystalline material consisting mainly of fullerene-60 with some fullerene-70 present. A recent X-ray diffraction image was obtained by MacKay et al.[227] using chromatographically purified fullerene-60 (Figure 34). This image is commensurate with a completely random mix of HCP and FCC arrays of fullerene-60 molecules. Fleming et al.[238] obtained purely FCC structured crystals from vacuum sublimed material. The implication is that interstitially trapped solvent probably stabilizes the mixed FCC/HCP crystals. It appears that fullerene-60 spheres are rotating in the lattice[231] and that when rotation ceases at low temperature the crystals are still disordered at the atomic level.[221,222,238]

A most interesting study as far as theoretical chemistry is concerned is that of Lichtenberger et al.[239,240] who measured the photoelectron spectrum of fullerene-60 on a surface and in the gas phase (Figure 35). The results are in good agreement with the theoretical (DV)-Xα study of Hale[169] (Figure 23). The first IP of fullerene-60, 7.61 eV, is nicely consistent with the result obtained by Zimmerman et al.[101] and McElvany.[102]

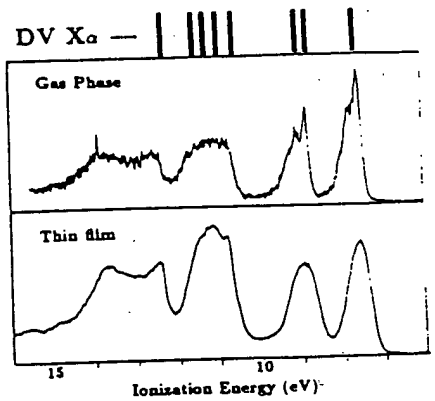

Figure 35. Gas phase (upper) and thin film (lower) He I valence photoelectron spectra of fullerene-60 obtained by Lichtenberger et al.[239,240] The DV-Xα results of Hale[169] (see Figure 23) which appear to be in good agreement with observation are indicated (reprinted from ref 239; copyright 1991 Elsevier Science Publishers).

Luffer and Schram[241] have made electron ionization mass spectrometric measurements on fullerene-60.

Several papers presented at a special symposium on the fullerenes (Nov 1990) have been collected together and published by Averback et al.[242] Some of the most important experimentally determined properties of fullerenes are presented in the Table I.

XI. Astrophysical Implications of C_{60}

Although low-temperature ion-molecule processes (Herbst and Klemperer[243] and Dalgarno and Black[244]) can account for most interstellar species, the long cyanopolyynes presented a problem. It was experiments which probed the possibility that carbon stars might be responsible for them[31,32] which revealed the stability of fullerene-60.[3] An important aspect of the experiments lay in the possibility of probing the conjecture of Douglas[40] that carbon chains might be responsible for the diffuse interstellar bands (DIBs). The DIBs are a set of interstellar optical absorption features of varying widths which have puzzled astronomers and spectroscopists since the mid-1930s. Herbig has published the definitive analysis of these features.[245,246] Many possible contenders for the carrier have been suggested, however no generally accepted explanation exists so far. This is strange as the species responsible is clearly abundant, chemically bound (i.e. not atomic), and must be quite stable in order to survive in the hostile interstellar environment or, if destroyed, be very efficiently reformed. The types of carrier appear to be few in number and must have very large electronic absorption coefficients.

The possibility that C_{60} might be the widely distributed in the Universe and particularly in the outflows from carbon stars was suggested when the original discovery of its stability was made.[3] It was also pointed out that the fullerene-60 surface might be an important site for the catalysis of interstellar reactions and perhaps it (*or a derivative*) might be responsible for such features as the DIBs. There is one key argument,[50,55-58] associated with the proposal that fullerene analogues (ionized or un-ionized, complexed or otherwise) may be

the carriers has that all previous suggestions do not: fullerene-60 and its analogues are unique in that they appear to survive the violent processes which occur when the atomic components of a chaotic plasma condense to form particles. Various aspects of this original conjecture, particularly with regard to possible derivatives such as intracage complexes both ionized and neutral, have been discussed[55-58] in general terms.

As far as the neutral fullerene-60 species in space is concerned, the negative results of searches based on the laboratory measurement[98] has been published by Snow and Seab[247] and Sommerville and Bellis.[248]

The conditions in the ISM are such that a large fraction of any fullerene-60 molecules present is likely to be ionized and thus it has been pointed out that the spectra of ionized fullerenes such as C_{60}^+ or fullerene analogues (such as the cage complexes $C_{60}M^+$) might be responsible for some astrophysical features.[55,57] Léger et al.[249] and Joblin et al.[250] have taken up the C_{60}^+ proposal and considered it further.

Complexed species (section VIII) in the interstellar medium are particularly interesting as any C_{60} present is likely to be ionized and probably have something stuck to its surface. As the DIBs exhibit features reminiscent of matrix spectra, the possibility that intracage complexes[55,57,201-203] as well as the extracage complexes[202] might be responsible has been discussed. Heymann[200] has considered the He intracage complexes and Ballester et al. other likely species containing O, Na, etc.[201] Kroto and Jura[202] draw particular attention to the fact that the charge transfer bands of the $(C_{60}M)^+$ intracage complex and the van der Waals extracage complex $(C_{60})^+$·M (M = alkali, alkaline earth, or other element) are likely to be very strong. Particularly interesting are possible relationships that charge-transfer transitions might have with the DIBs and perhaps also the strong unassigned 2170 Å absorption feature which has puzzled astronomers for over seven decades. Hoyle and Wickramasinghe[251] suggested that C_{60} itself might explain this feature and further calculations relating to this possibility have been discussed by Braga et al.[167] Rabilizirov[252] has also discussed these possibilities. Wright[253] has discussed the general optical/UV characteristics of fullerenes and concludes that the observed interstellar extinction is not consistent with the presence of significant quantities of spheroidal particles with graphite-like outer shells. In this respect the existence of the amorphous carbon surface layers surrounding the graphite cores of carbon microparticles may well be important.[116] From the UV/vis spectra obtained so far[4,215,216] it is clear that neutral fullerene-60 is not responsible for either the DIBs or the 2170 Å hump.

There are also some intriguing interstellar emission features in the IR, termed the unidentified infrared bands (UIBs), which have been assigned to PAH-like material by Duley and Williams,[254] Léger and Puget,[255] and Allamandola et al.[256] The assignment rests largely on the reasonable correspondence between the astrophysical frequencies and those of polycyclic aromatic molecules which are usually used for fingerprint identification of large PAHs. Balm and Kroto[257] have discussed the fact that, if the fullerene-60 concept is correct, PAH material in space is likely to be nonplanar. They point out that one feature, namely that at 11.3

The new results also offer possible new avenues of study as far as condensed carbonaceous matter in the cosmos is concerned. According to McKay et al.[258] caged carbon clusters may offer a plausible explanation of some of the isotope anomalies observed in the elemental analysis of carbonaceous chondrites particularly the ^{22}Ne anomaly. Clayton[259] has pointed out that condensation in the atmospheres of supernovae might explain the so-called Ne-E anomaly. McKay et al.[258] have suggested that this observation might be explained by encapsulation of ^{22}Na in fullerene cages or icospiral embryos during the dust formation phases that follow supernova and nova outbursts. Subsequently, the decay of ^{22}Na yields an encapsulated ^{22}Ne atom. Zinner et al.[260] have pointed out that isotope anomalies are only to be found in spheroidal carbon grains. So far the only evidence that C_{60} might exist in space is an unconfirmed report by Anderson.[261]

XII. Conclusions

It took some 15 or so years before the imaginative theoretical conjectures of Osawa and Yoshida[13,14] and Bochvar and Gal'pern[17,18] were realized in the discovery of the stability of the C_{60} mass spectrometric signal[3] in 1985. A further period of five years elapsed during which time many experimental measurements and theoretical studies were made. By-and-large the theoretical work (section VIII) substantiated the idea that buckminsterfullerene should be stable. As time elapsed the weight of circumstantial evidence grew and ultimately became convincing. The key observations include:

(1) Detection of monometallic complexes indicated that atom encapsulation was feasible.[7,96]

(2) Further cluster beam studies showed 60 to be a magic number whether the carbon species was positively or negatively charged or neutral.[64,66,52]

(3) Reactivity studies showed the molecule to possess an inertness that was consistent with closure and the absence of dangling bonds.[103,96]

(4) The pentagon isolation principle explained the observation of C_{60} as the first magic number and C_{70} as the *second*.[8,9] Thus it was shown that the fullerene hypothesis rested on the observation of two magic numbers and not just one. Further refinement of the geodesic principle explained other observed magic numbers.[8,9]

(5) Large fullerene networks were found to possess quasiicosahedral structures and thus related giant concentric cage species[108] appeared to explain the infrastructure of the carbon microparticles observed by Iijima.[109,110]

(6) Photoelectron measurements of Yang et al.[99] were also quite consistent with the fullerene conjecture.

These and other studies (discussed in sections V–VII) thus had laid the background against which the critical infrared observation of Krätschmer et al.[5,74] was made. They were led to make this observation by considering that some intriguing optical features observed in 1982 might be due to buckminsterfullerene. These observations were followed up by Krätschmer, Lamb, Fostiropoulos, and Huffman[4] and Taylor et al.,[6] and the results have revolutionized the field in that now the material can be made in quantity and the properties of

It is interesting to note that the motives for the experiments which serendipitously revealed the spontaneous creation and remarkable stability[3] of C_{60} were astrophysical. Behind this goal lay a quest for an understanding of the curiously pivotal role that carbon plays in the origin of stars, planets, and biospheres. Behind the recent breakthrough of Krätschmer et al. in producing macroscopic amounts of fullerene-60, lay similar astrophysical ideas.[4] It is fascinating to now ponder over whether buckminsterfullerene is distributed throughout space, and we have not recognized it, and that it may have been under our noses on earth, or at least played an important role in some very common environmental processes, since time immemorial.

The material is already exhibiting novel physical and chemical properties and there can be little doubt that an exciting field of chemistry and materials science, with many exciting applications has opened up. One of its most important properties is its ability to accept electrons. The low-lying LUMO causes it to be a soft electrophile.

It is perhaps worthwhile noting that C_{60} might have been detected in a sooting flame decades ago and that our present enlightenment has been long delayed. How serious this delay has been only time will tell; however, already fullerene chemistry is a vibrant field of study and the prospects for new materials with novel properties is most promising. Certainly, a New Round Postbuckminsterfullerene World of carbon chemistry appears to have been discovered, almost overnight. It should not be long before the molecule becomes a standard in textbooks; indeed construction procedures for fullerene-60 and giant fullerenes are to be found in the educational literature.[126,252]

Warning

The UCLA group has pointed out the importance of treating the material with great caution at this time when so little is known about it.[253] Its ability to catalyze the formation of singlet oxygen and its novel chemical behavior inevitably suggest the possibility that the fullerenes might be carcinogenic. Particular care should be taken to ensure that the dust is not inhaled during preparation of the soot itself.

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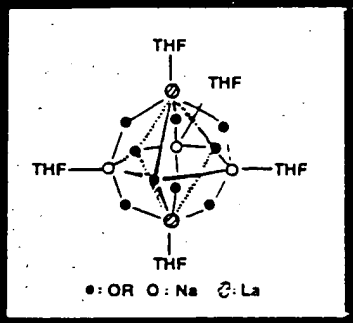
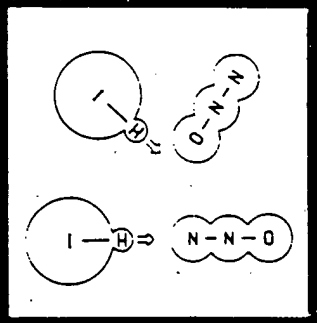
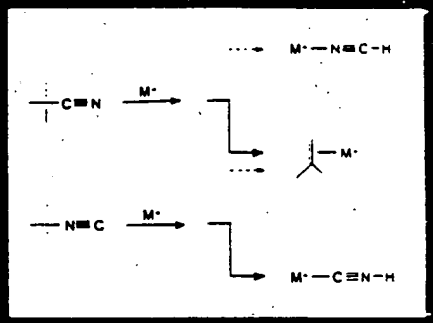
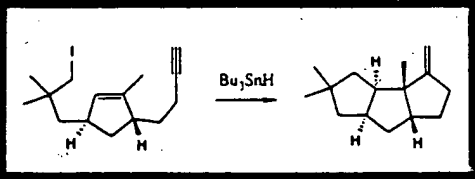
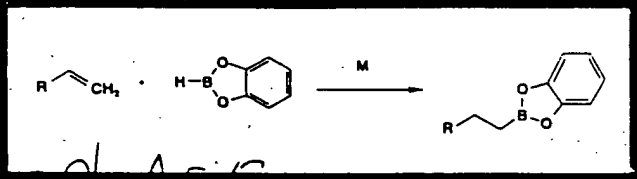
CHEMICAL REVIEWS

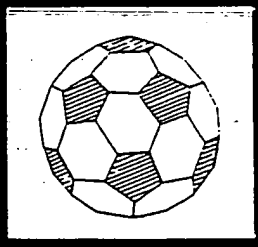


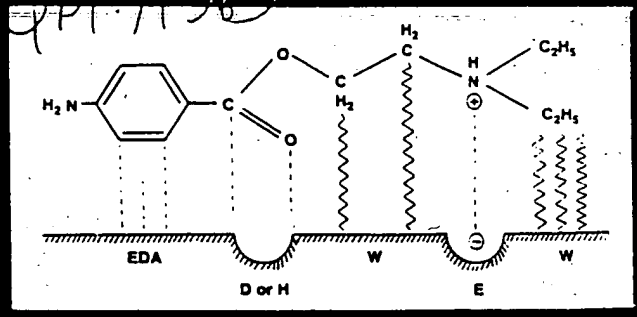












ANGEWANDTE CHEMIE

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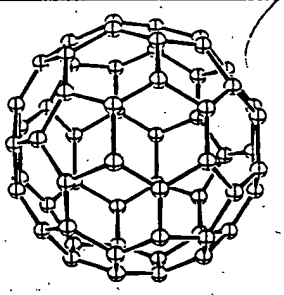
31 (1992) 2

The cover picture shows a section of a high-frequency oven used in a novel synthesis of fullerenes. The reaction zone (at approximately 2800 °C, the light is dimmed by the soot beginning to deposit) is depicted at the start of the fullerene production. The inductor, boron nitride insulation tube, quartz tube, and initial formation of smoke can be seen. More about the novel efficient synthetic method is reported by M. Jansen and G. Peters on page 223. The boom in fullerene chemistry continues. The third in a series of highlights on the important recent results (previous updates were published last year in the January and June issues) will appear in the next issue. An overview of the preparations, properties, and reactions of C_{60} is planned. This issue includes two highlights on silicon clusters including Si_{60} (p. 173). a communication on $He@C_{60}$ (p. 183), and, last but not least, an exciting account by H. Kroto on the start of the fullerene story (p. 111).

Review Articles

A "round organic chemistry" has burgeoned this last year following the development of an efficient means of producing fullerenes in 1989/1990. One of the protoganists in the fullerene story describes in a lively personal style how this fascinating new chemistry came about. In this thriller he points out that the discovery of C_{60} in 1985 did not result from an applications-oriented search but rather from basic research and scientific curiosity.



C_{60}

H. W. Kroto*

Angew. Chem. Int. Ed. Engl. **1992**, *31*, 111...129

C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

Almost atomic resolution is achieved today in techniques for studying monomolecular Langmuir films of amphiphilic molecules. Synchrotron X-ray sources providing well-collimated, high-intensity radiation make this possible. In this review the principles and methods used to study thin films are discussed. In these investigations, for instance, a strong influence from solute molecules or ions in the subphase on the crystallinity of the monomolecular layer was revealed: whereas α-glycine increases the crystallinity of a fluorocarbon monolayer, β-alanine decreases it. Possible explanations for the phenomena are also presented.

D. Jacquemain, S. G. Wolf, F. Leveiller, M. Deutsch, K. Kjaer,* J. Als-Nielsen,* M. Lahav,* L. Leiserowitz*

Angew. Chem. Int. Ed. Engl. **1992**, *31*, 130...152

Two-Dimensional Crystallography of Amphiphilic Molecules at the Air–Water Interface

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C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

By Harold W. Kroto*

In 1975–1978 the long-chained polyynylcyanides, HC_5N, HC_7N, and HC_9N were surprisingly discovered in the cold dark clouds of interstellar space by radioastronomy. The subsequent quest for their source indicated that they were being blown out of red giant, carbon stars. In 1985 carbon-cluster experiments aimed at simulating the chemistry in such stars confirmed these objects as likely sources. During these cluster studies a serendipitous discovery was made; a stable pure-carbon species, C_{60}, formed spontaneously in a chaotic plasma produced by a laser focused on a graphite target. A closed spheroidal cage structure was proposed for this molecule, which was to become the third well-characterized allotrope of carbon and was named buckminsterfullerene. It has taken five years to produce sufficient material to prove the correctness of this conjecture. There may be a timely object lesson in the fact that exciting new and strategically important fields of chemistry and materials science have been discovered overnight due to fundamental research, much of which was unable to attract financial support, and all of which was stimulated by a fascination with the role of carbon in space and stars. In this account, interesting aspects of this discovery, its origins, and its sequel are presented. The story has many facets, some of which relate to the way scientific discoveries are made.

Molecules with Unsaturated Carbon Bonds

In the early 1970s, the chemistry of carbon in unsaturated configurations became the prime research focus for my group at the University of Sussex.[1] We were interested in free unstable species and reaction intermediates containing C-S, C-P, C-Si, or even C-C multiple bonds. The work originated from an abortive attempt to produce thioformaldehyde ($H_2C{=}S$) by photolysis. However, we switched immediately to thermolytic activation after I heard a lecture in which Don Johnson (from the U.S. National Bureau of Standards in Washington, D.C.) described how he and Powell had made this compound[2] by passing MeSSMe vapor through a quartz tube heated simply by a bunsen burner! This approach worked beautifully; we produced numerous other new compounds containing the C=S moiety such as thioethanal and thioketene by thermolysis of specially synthesised precursors, and characterized them mainly by microwave and photoelectron spectroscopy.[1] These sulfur species possessed a distinctive odor, and I for one have sympathy with the citizens of Freiburg who, according to Noller,[3] forced Baumann and Fromm to abandon their work on these compounds. We gave up our work on seleno analogues for similar reasons after detecting selenopropanal! After success with sulfur/carbon compounds we jumped, in the spirit of Mendeleev, to the next element in the second row of the periodic table, phosphorus. The first phosphaalkenes, $CH_2{=}PH$ and $CH_2{=}PCl$,[4] were produced in 1976 in a joint project with John Nixon; several more followed.[1] Simultaneously, Becker in Germany made $PhP{=}C(t\text{Bu})OSiMe_3$.[5] At this stage I envisaged a simple possible solution to the problem which had been on my mind

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since 1964, namely to ascertain whether derivatives of Gier's beautiful molecule HC≡P[6] could be made. I had been fascinated with HC≡P since the day I arrived as a postdoc at the National Research Council (NRC) laboratory in Ottawa and heard Takeshi Oka (who was then also an NRC postdoc) enthuse over a spectrum of this molecule which Kelvin Tyler (another NRC postdoc) had just obtained.[7] It seemed to me that the chemistry of HC≡P and its analogues must parallel that of the nitriles. Transition-metal complexes could probably be prepared, and cycloadditions to generate phosphorus-containing rings would be feasible.[8, 9] The simple approach worked very well, and we produced the first phosphaacetylene derivative, $CH_3C{\equiv}P$,[10] by thermolysis of $EtPCl_2$ (provided by R. Schmutzler). We followed this breakthrough with the syntheses of other XC≡P species (X = Hal, Ph, N≡C, N≡C−C≡C, etc.[11]). It is most satisfying that, as I had originally conjectured in 1964, the phosphaalkynes (and the phosphaalkenes) have subsequently been exploited by ourselves and other groups as synthetic building blocks.

In parallel with our studies of compounds made up of second-row elements and carbon we probed molecules containing chains with C−C multiple bonds. My fascination with such chains developed very early on in a study of the peculiar molecule, carbon suboxide O=C=C=C=O (one subject of my Ph.D. work at Sheffield in the early 1960s with my supervisor Richard Dixon). This stimulated my curiosity in extended carbon chains and the unusual flexibility which they often exhibited; a preoccupation with such molecules has continued to this day. When I flash-photolyzed C_3O_2 a year or two later at the NRC, I ended up with a cell full of black soot and a magnificent spectrum of the C_3 molecule, whose enigmatic patterns had finally been deciphered by Gausset et al.[11] Almost everything about these carbon chains seemed idiosyncratic, and I stored such observations up for the future. These memories were reawakened in the early 1970s by David Walton's work on polyynes at the University of Sussex. David had developed elegant methods for synthesizing long-chain polyynes, based upon silyl-protection techniques which he pioneered in acetylene chemistry.[12–14] He and his students had made the parent 24 carbon-atom species in minute quantities in solution and

H−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−C≡C−H

even a 32 carbon-atom (silyl-protected) polyyne.[13] These chains were precisely what was needed for a study of vibration–rotation dynamics—a topic which had attracted my interest. In my mind they conjured up an image of a microscopic quantum-mechanical cheerleader tossing a very bendy bamboo baton high into the air—and then attempting to catch the violently flexing and turning baton it as it descended. The obvious first compound for microwave study was the cyanopolyyne, HC_5N, because of its expected enormous dipole moment. Walton devised a synthetic route; Anthony Alexander, a "Chemistry by Thesis" student (editorial comment: for an explanation see the acknowledgements at the end of the review), successfully prepared it and measured its microwave spectrum in 1974.[15] This was a wonderful achievement for an undergraduate and a very important one for me, since it was the first molecule to be characterized on our newly acquired microwave spectrometer.

Fig. 1. The dark clouds in Taurus from Barnards 1927 survey, *Atlas of Selected Regions of the Milky Way*, (Ed.: E. B. Frost, R. Calvert), Carnegie Institute, Washington, D.C., 1927. Heiles's Cloud 2 is in the left-hand bottom corner as indicated by coordinate markers.

At about this time spectacular advances were being made in molecular radioastronomy. The black clouds which are smeared across our Milky Way galaxy (Fig. 1) were found to possess long-hidden dark secrets. Townes and co-workers[16] opened the Pandora's box in 1968 and revealed that the clouds are full of identifiable molecules. Astronomers suddenly realized what a key role molecules played in the

Harold Kroto, born in 1939, studied in Sheffield from 1958 to 1964 and received his Ph.D. for his research in the electronic spectroscopy of free radicals with R. N. Dixon. After three years of postdoctoral research at the National Research Council in Ottawa and Bell Laboratories, he started his academic career in 1967 at the University of Sussex in Brighton, where he became full professor in 1985. The most recent distinction Kroto has received is a Royal Society Research Professorship (1991). Since 1990 he has been chairman of the editorial board of the Chemical Society Reviews. His research interests include the spectroscopy of unstable species, carbon and metal clusters and microparticles, as well as interstellar molecules and circumstellar dust. Graphic design is his other passion.

intimate gas dynamics involved in the birth of stars and planets. Apart from well-known species such as ammonia, water, and ethanol—enough for 10^{28} bottles of schnapps in Orion alone—Bill Klemperer ingeniously identified the HCO^+ ion (protonated CO)[17] which had not previously been detected in the laboratory. Thus space served not only as a playground reserved for astronomers, but it now presented chemists with a novel piece of apparatus, indeed a colossal new spectroscopic sample cell, containing a plethora of exotic molecules in a wide range of physico-chemical environments.[18] Shortly after Turner[19] had detected HC_3N by microwave frequencies, I wrote to Takeshi Oka at the NRC; my group had recorded the analogous frequencies of HC_5N, and I wanted to search for the molecule in space. Takeshi and I had worked (1964–1966) in the same laboratory at the NRC during the golden years of that research organization.[*] He replied saying that he was "very, very, very, very, very much interested".

In November 1975 the search for radio waves of HC_5N (with Canadian astronomers Lorne Avery, Norm Broten, and John MacLeod) resulted in the successful detection of a signal from Sgr B_2, a giant cloud of molecules near the center of the galaxy.[20] Although we had been hopeful, we were surprised by our discovery since it had seemed such a long shot. In 1975 molecules with more than three or four heavy (C, N, or O) atoms were assumed to be far too rare to be detectable. However, having found HC_5N in space, we thought that HC_7N might also be present. Walton devised a synthesis of HC_7N, and graduate student Colin Kirby managed the very difficult problem of making it and measuring its spectrum.[21]. By the time Colin (in England) finally succeeded in recording the vital frequency, we were actually working on the radio telescope, since our allotted observing session had already started. Colin telephoned my wife, who wrote the value on an envelope (Fig. 2 left). She then tele-

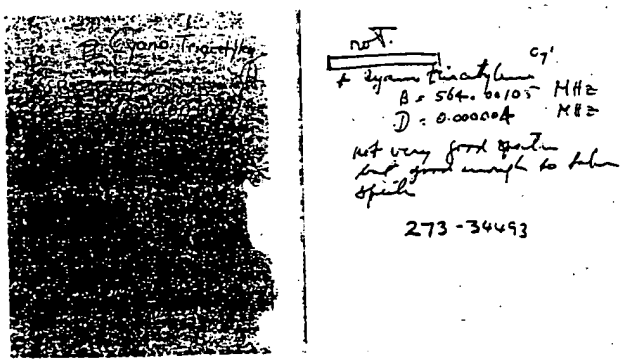


Fig. 2. The envelope (left) and intermediate note (right) with the precious experimental data from which the frequency of HC_7N in space was determined.

phoned Fokke Creutzberg, a friend in Ottawa, who also noted it carefully (Fig. 2 right) and transmitted it to us at the telescope site in Algonquin park (Fig. 3). The next few hours were high drama. We dashed out to the telescope and tuned the receiver to the predicted frequency range as Taurus

[*] Under the guidance of Gerhard Herzberg the NRC had become the Mecca for spectroscopists, and it was here that Cec Costain introduced me to the delights of microwave spectroscopy.

Fig. 3. The 46 m radiotelescope in Algonquin Park, Ontario, Canada with which the long-chain carbon molecules in space were detected.

(Fig. 1) rose above the horizon (perfect timing). We tracked the extremely weak signals from the cold dark cloud throughout the evening. The computer drove the telescope and stored incoming data, but to our frustration we could not process the data on-line while the telescope was running. The system did, however, display individual ten-minute integrations, and as the run progressed we watched the oscilloscope for the slightest trace of the predicted signal in the receiver's central channel. During the course of these ten-minute snapshots, we gradually concluded that the central channel signal was possibly higher on the average than nearby ones. Desperate for even the faintest scent of success, we carried out a simple statistical analysis in order to determine whether the signal level of the channel was greater than the noise. As the night wore on we became more and more excited, convinced that the signal was significantly more often high than low; we could hardly wait for Taurus to set. By 1:00 a.m. we were too excited and impatient to wait any longer, and shortly before the cloud vanished completely, Avery stopped the run and processed the data. The moment when the trace in Figure 4 appeared on the oscilloscope was one of those that scientists dream about and which, at a stroke, compensate for all the hard work and the disappointments which are endemic in life. The circumstances of this discovery—the arrival of the value of the microwave fre-

Fig. 4. The first oscilloscope trace of the radio signal emitted by interstellar HC_7N in Heiles's Cloud 2 in the constellation of Taurus (see the coordination markers in Fig. 1).

quency from the UK just in the nick of time, the gradual growth of the conviction that there might be a signal in that central channel of the receiver, and then finally the revelation that we (Fig. 5) had detected an enormous molecule in space[22]—made for a truly cathartic scientific experience. (Modern on-line data processing would have diminished the experience). Obviously, the next candidate was HC_9N, but

Fig. 5. The team at the NRC laboratory just after the detection of HC_7N in space (from left): Avery, Oka, Broten, MacLeod, and Kroto.

its synthesis was a daunting task. Fortunately, Oka developed a beautifully simple extrapolation technique with which he predicted the radio frequencies of HC_9N. Almost unbelievably, we detected this molecule as well![23] Bell et al. later detected even $HC_{11}N$.[24]

The Search for the Source of Carbon Chains in Space

It is not so obvious today, but in 1975–1978 such long-chain molecules were a totally new and unexpected component of the interstellar medium. How such species came to be present was not at all clear. I felt that it was not sufficient just to have co-discovered them; I really wanted to solve the puzzle of how they got there in the first place, and indeed what they were doing there anyway. After all, everything in nature seems to have some role to play. The search for the source of these compounds became something of a preoccupation (even an obsession). By the early 1980s I was convinced that the ion–molecule reactions which Eric Herbst and Bill Klemperer,[25] and Alex Dalgarno and John Black[26] had devised, and which accounted beautifully for almost all other interstellar molecules, really could not explain the origins of chain molecules.[1, 18] It gradually became clear to me that red giant, carbon stars must hold the key. Particularly interesting was the spectacular infrared object IRC+10216, discovered by Eric Becklin and his colleagues,[27] which pumps vast quantities of chains and grains out into space. I wondered about this red giant and the fact that it was shrouded in grains and chains, which were formed at roughly the same time,[1, 18] and whether "the long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2, and C_3, which are well known, and particles with high carbon content such as soot".[1] Perhaps some symbiotic chain/dust chemistry was involved.

The First Visit to Rice University (Easter 1984)

The foregoing account sets out the background for my thoughts about the role of carbon in space prior to my trip to Rice University in Texas during Easter 1984 to visit Bob Curl. Almost the first thing that Curl told me was that I should visit his colleague, Rick Smalley. He enthused over a very recent result obtained by Smalley and his co-workers, who had analyzed the spectrum of the SiC_2 and had shown the molecule not to be linear, as some might have expected, but triangular.[28] (The analogous C_3 species is linear, although only just.[11]) I visited Smalley's laboratory and saw the laser vaporization cluster-beam apparatus which he and his co-workers had recently developed. This powerful technique enabled the mass-spectrometric study of stable clusters formed in a helium-entrained plasma, produced by a pulsed laser focused on a solid target. In this particular experiment silicon carbide was vaporized and the electronic spectrum of SiC_2 observed.[28] I was much impressed by the result but even more by the experimental technique.[29] This method was clearly a major breakthrough in cluster science, since it made refractory clusters accessible for detailed study for the first time. I had already heard of it, but to see the apparatus in operation was quite fascinating. The result of the SiC_2 experiment was particularly interesting to me, because it was consistent with some unusual theoretical results for >Si=C< species[30] obtained at Sussex in collaboration with John Murrell some years earlier. What excited me most, however, was the thought that by simply replacing silicon carbide with graphite, it should be possible to simulate the type of chemistry which takes place in the atmosphere of a carbon star and produce the long carbon chains. As the day wore on I became more and more convinced that the technique was perfect for this purpose and that evening discussed it with Curl. Because of his interest in microwave spectroscopy, he was immediately enthusiastic, and we made plans for a joint project in the hope that Smalley would also be interested. Perhaps we could detect chains with as many as 24–32 carbon atoms related to Walton's polyynes or Hintenberger's equally amazing pure-carbon species (C_{33} etc.), which were detected by mass spectrometry in the early 1960s in a carbon arc.[31] I dreamt that one day it might be possible to detect a chain molecule such as $HC_{33}N$ (which is as long as the chains that Walton had made in a test tube) in space. Curl was particularly excited by the prospect that we could check out an interesting idea of the late Alec Douglas,[32] namely, that carbon chains might be carriers of the famous Diffuse Interstellar Bands—a set of absorption features[33] which have puzzled astronomers and spectroscopists for more than six decades. Because the project was not considered a priority by the cluster group at Rice University at that stage, it had to await a convenient slot in their program.

In the interim, a group at Exxon carried out the basic graphite-vaporization experiment. In the summer of that year (1984) they published a fascinating result: the discovery of a totally new family of carbon clusters C_{30}–C_{190}[34]—

much larger species than those prepared by Walton et al.[12-14] or observed by Hintenberger.[31] This exciting discovery was peculiar because only even-numbered clusters were detected. It is important to note that at this juncture no specific cluster was perceived to be special. In August 1985 (almost 18 months after my visit) Curl telephoned to say that carbon experiments were at long last imminent. He asked whether I wanted to come to Houston to participate or if they should carry out the experiments and send the data to me. One thing was certain in my mind: I had not waited this long to have my experiments carried out by others in my absence; I wanted to do them myself and to direct the operation personally. Therefore I packed my bags and at my wife Marg's expense arrived at Rice University within days.

Second Visit to Rice University—The Discovery of C_{60}

Silicon and germanium cluster studies were on the Rice plate in August 1985 because of their implications for semiconductors. Such experiments were considered to be important because the results might have useful applications (!) The carbon project, on the other hand, was thought to have no possible application (other than for astronomy) and was to be completed quickly, causing as little delay to the semiconductor study as possible. Preliminary measurents on carbon had already been carried out, and the Exxon spectra had been reproduced; nothing untoward was noticed. As soon as I arrived (August 28th) I presented a lengthy informal seminar on everything I knew about carbon in space, stars, and soot. My experiments started on Sunday, September 1st, 1985. I worked in the laboratory alongside two research students, Jim Heath and Sean O'Brien—an exhilarating experience; Yuan Liu was also involved. We toiled late into the night, varying the clustering conditions and monitoring the reactions of the carbon clusters with hydrogen, oxygen, and ammonia—gases which I thought would give rise to polyynylcyanides and other chain molecules. They did! The experiments thus immediately confirmed that the chemistry in red giant stars could be responsible for interstellar carbon chains. Curl and Smalley paid frequent visits to the laboratory. As the experiments progressed it gradually became clear that something quite remarkable was taking place: As we varied the conditions from one run to the next, we noticed that a peak at 720 amu[*] (corresponding to a C_{60} species) behaved in a most peculiar fashion. Sometimes it was completely off-scale; at other times it was quite unassuming. The spectrum recorded on Wednesday, September 4th, 1985 was astounding (Fig. 6). Our reactions were noted in the laboratory record book (Fig. 7a), and I annotated my copy of the printout (Fig. 6). From that point onwards the idiosyncratic behavior of this peak was followed very, very closely (Fig. 7b). When this result appeared, the carbon project—

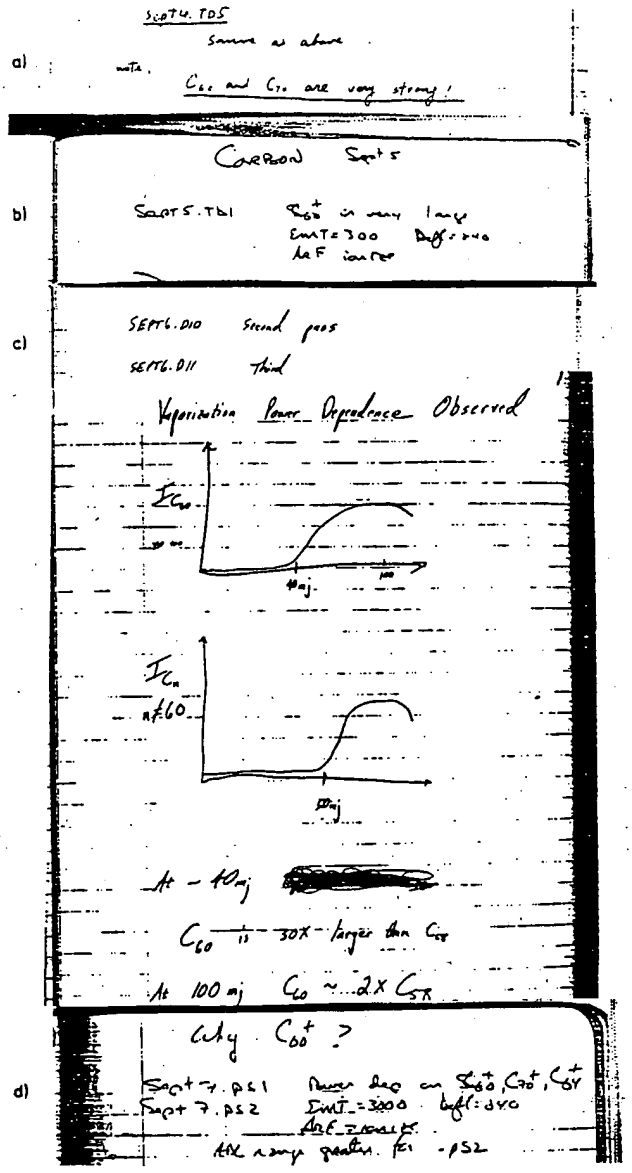


Fig. 7. Entries by Heath, Liu, and O'Brien in the Cluster Laboratory Notebook from the period September 4–7, 1985 when key experiments were carried out at Rice University. a) September 4th: First recorded note that C_{60} and C_{70} were very strong (see also Fig. 6). b) September 5th: C_{60} signal again very strong. c) September 6th: Record of first experiments which specifically aimed at optimization of the conditions for production of a dominant C_{60} signal ("C_{60} is 30 × larger than C_{58}.") d) September 7th: Further power-dependence studies.

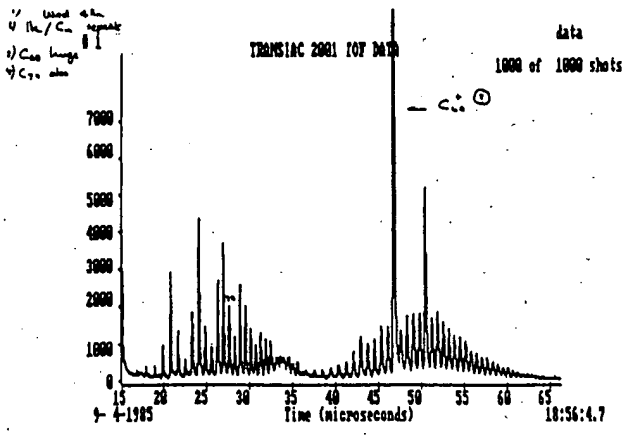


Fig. 6. Annotated time-of-flight (TOF) mass spectrum of carbon clusters produced on Wednesday, September 4th, 1985, the day on which the dominance of the C_{60} signal was first recorded (see also Fig. 7a).

[*] Editorial note: amu = atomic mass unit. According to *Quantities, Units and Symbols in Physical Chemistry* (Ed.: Int. Union of Pure and Applied Chemistry), Blackwell, Oxford, 1989 (Chapter 2.10), amu is the symbol for the unified atomic mass unit m_u and the unit u. In this review the unit amu which is still encountered frequently is used.

for the first time—engendered general interest, and by mutual agreement continuation of the semiconductor program was delayed so that we could concentrate on the remarkable phenomenon which we had uncovered. As the weekend approached our actions, thoughts, and conversations turned more and more to the phenomenon. What might this special "wadge" of carbon be? Smalley had never come across this British term for a cluster and liked it so much that he started to refer to C_{60} as the "Mother Wadge"; the omnipresence of the cluster led me to call it the "Godwadge". On Friday, September 6 during a group meeting, Curl suggested that we should concentrate on identifying the conditions under which the 720 amu peak was most prominent. O'Brien and Heath agreed to work shifts during the weekend. Experiments aimed specifically at optimizing the signal were carried out that same evening, and conditions were immediately found under which C_{60} peak was 30 times stronger than the adjacent C_{58} signal (Fig. 7c). After further optimization (Fig. 7d) the striking spectrum (Fig. 8) was finally obtained. C_{70} is also prominent!

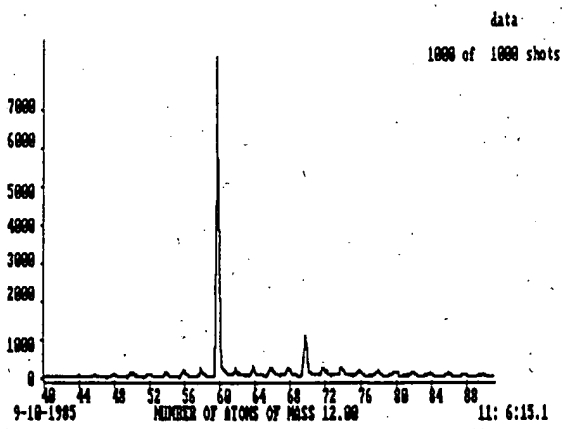


Fig. 8. TOF mass spectrum of carbon clusters under the optimum conditions for the observation of a dominant C_{60} signal.

The Structure of C_{60}(?)

What on earth could C_{60}(?) be? In the days following our discovery of C_{60} (Fig. 6), the signal began gradually to dominate our results as well as our thoughts and conversation. The quest for a structure which could account for this precocious wadge of carbon led to numerous, synergistic [Editorial comment: R. Buckminster Fuller's architectural constructions were based on a vectoral geometry which he called energetic—synergetic geometry. This was founded on a natural philosophy, according to which nature constructs systems of forces such that the maximal strength can be obtained from the minimum effort in construction.] discussions among all five members of the team during those days. The deliberations were particularly intense on Monday, September 9th. As this day wore on and all the ideas which had surfaced during the period were assessed and reassessed, a consensus grew that C_{60} might be some sort of spheroid. One possibility we considered was that the laser had blasted flakes of hexagonal carbon from the graphite surface, and that these hot graphite-like networks had somehow wrapped themselves up into closed cages, thus eliminating the dangling edge bonds and making the cage unreactive. This idea had instant appeal for all. For me this concept brought back vivid memories of Buckminster Fuller's geodesic dome at EXPO '67 in Montreal (Figs. 9 and 10). I had actually

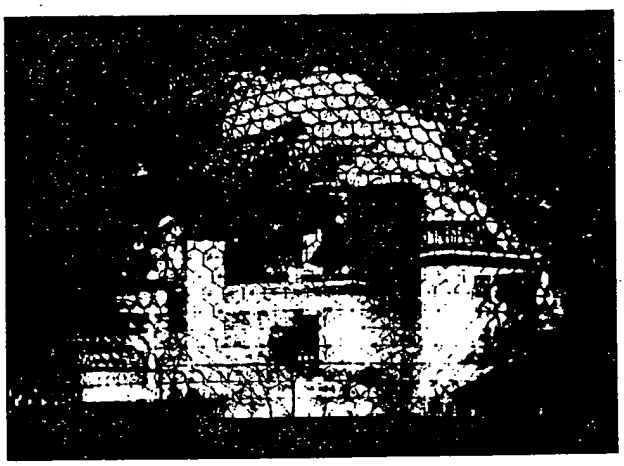


Fig. 9. Photograph (by Michel Proulx) of the geodesic dome designed by Buckminster Fuller for the U.S. exhibit at EXPO '67 in Montreal (taken from *Graphis* **1967**, *132* 379). One of the pentagons necessary for closure is discernable in this photograph.

been inside this remarkable structure at that time and remembered pushing my small son in his pram along the ramps and up the escalators, high up among the exhibition stands and close to the delicate network of struts from which the edifice was primarily constructed. This experience had left an image in my mind which could never be erased. I had collected numerous photographs of the dome from magazines over

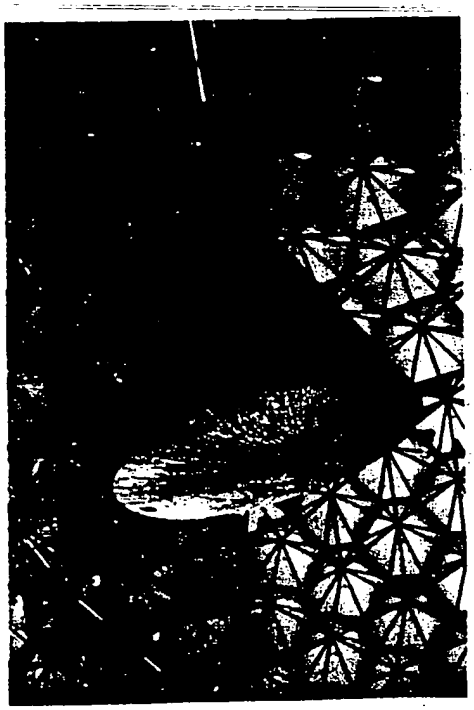
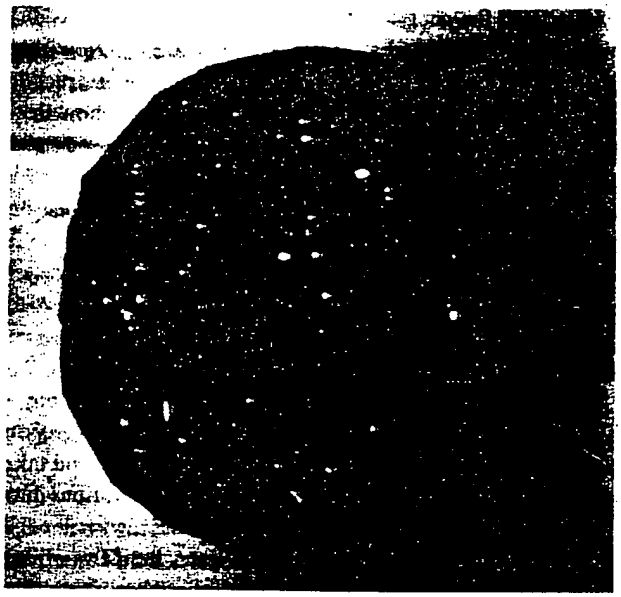


Fig. 10. Photograph (by Robin Whyman) of the inside of the EXPO '67 dome in Montreal. One of the pentagons necessary for closure is clearly visible in the middle section, as is the way in which the strut lengths have been adjusted to achieve a smooth round shape.



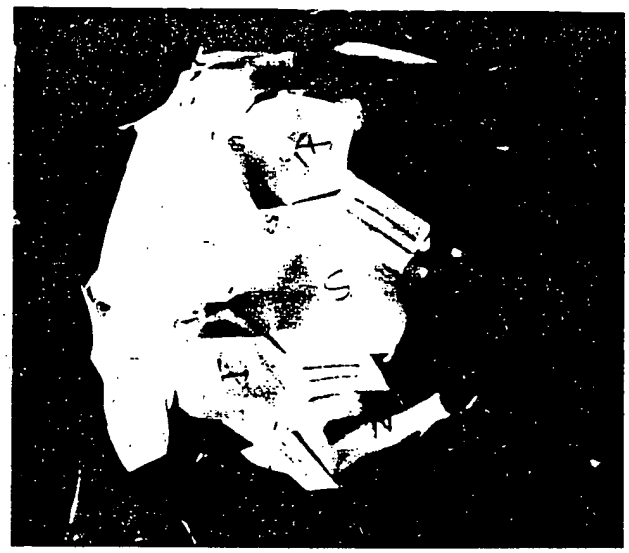


Fig. 11. The two cardboard polyhedra which played key roles in our search for the structure of C_{60} (see text). Left) stardome map of the sky (Buckminster Fuller patented t-icosahedral and other polyhedral world-map projections); right) Smalley's model with 60 vertices and 12 pentagonal and 20 hexagonal faces.

the years from Life, Paris Match, and Graphis. Particularly striking were those in my favorite graphic art and design magazine, Graphis, to which I had subscribed since my university days. As I remembered it, the Graphis pictures (Fig. 9) showed that the dome consisted of a plethora of hexagonally interconnected struts. Indeed, the dome had actually initiated my interest in some of Buckminster Fuller's other projects; I had even been in the process of writing to him with a view to working with him on the organized growth of massive urban structures. However, I did not pursue this, because I was offered a permanent academic position at Sussex at just that time.

As far as C_{60} was concerned, I wondered whether Buckminster Fuller's domes might provide some clue. Smalley also strongly favored some sort of spheroidal structure and suggested that we borrow a book from the Rice University library. We obtained a book by Marks[35] in which geodesic domes of all kinds were described. In addition I had one or two other structural proposals which intrigued me: One was a four-deck model 6:24:24:6 (two coronene-like sheets sandwiched between two benzenoid ones) with a roughly spheroidal shape. It contained 60 atoms, and its symmetry suggested that the dangling bonds might be somewhat deactivated. However, I really could see no reason why this species would be as unreactive as C_{60} appeared to be; a closed-cage solution would certainly be more stable. A second image came to mind several times, most vividly on this particular Monday. This was of a polyhedral cardboard stardome (Fig. 11 left) which I had constructed many years before when my children were young. This map of the stars in the sky was tucked away in a cardboard box (that universal quantum of storage) downstairs in my home far away in England. I itched to get my hands on it and even described its features to Curl at lunch time. I remembered cutting out not only hexagons but also pentagons. I wondered whether I should telephone my wife to ask her to count the vertices in order to ascertain whether, as I half-suspected, they totaled sixty.

The Mexican Restaurant

I was due to return to the UK the next day, so that evening (Monday, September 9th) I thought we should celebrate our extraordinary discovery. I invited the group out to dinner at what had become our favorite Mexican restaurant. During the meal the conversation was naturally dominated by C_{60}(?). We again considered all the ideas which had come up in our deliberations during the days that had passed since the signal had first been noticed. We agreed unanimously on a *closed cage* structure. We talked about Buckminster Fuller's domes, Smalley, about chicken-wire cages, and I reiterated the essentials of the stardome—its spheroidal shape, hexagonal faces, and, in particular, the pentagonal faces. Smalley expressed an interest. After the meal other members of the group went home; I returned to the laboratory in order to study the Marks' book on Buckminster Fuller, but I could not find it. I again considered telephoning home about the number of vertices in the stardome. But it was now far too late since it was well after midnight in the UK.

Very early the next morning Curl telephoned to say that Smalley had experimented with paper models based on the stardome characteristics I had mentioned the previous day. Smalley had come up with something bigger than anything he (Curl) had ever been involved with before. When I got to the laboratory and saw the paper model (Fig. 11 right) which Smalley had constructed during the night I was ecstatic and overtaken by its beauty. It seemed identical to the stardome as I remembered it, and I was quietly pleased that my conjecture had been right all along. Heath and his wife Carmen had also experimented with a geodesic structure modeled out of jelly beans and toothpicks; it was not quite so convincing.[36]

In summary, the quest for a rational explanation of the dominant line in the mass spectrum had reached a climax on Monday, September 9th. Ideas were suggested, refined, or critized in earnest throughout that final day. Buckminster Fuller's domes were invoked, Marks' book was consulted, and the stardome's pentagonal faces introduced at midday

and again in the evening; Smalley and the Heaths experimented further with models during the night after our meal. All this took place in a matter of hours, leaving no time for anything important—other than perhaps Marks' book—to "slip through the cracks".[37] It was most satisfying that synergistic (a Fullerism) teamwork had been involved in the experimental observation as well as in the positing of the structure.

I delayed my flight home for one extra day (until Wednesday, September 11th) in order to help to write the publication. At one point Heath was sitting at Smalley's desk when the telephone rang. A mathematician, whom Smalley had consulted earlier to ask about the structure, informed Heath, "Tell Rick—it's a soccerball!" Almost unbelievably, until that moment, none of us had realized that the C_{60} structure we were proposing had the same symmetry as the modern soccer-(USA) or football (rest of the world). I do not know how I could have been so blind—my only (feeble) excuse was that the modern football was introduced after I ended my serious soccer-playing days. The other members of the team could be excused, since a structure related to the American football really was an unlikely contender, at least at that stage. We immediately purchased a real football and our five-a-side team posed for a photograph (Fig. 12). I also

Fig. 12. The five-a-side Rice/Sussex football team (from left): O'Brien, Smalley, Curl, Kroto, and Heath.

photographed Smalley's paper ball (Fig. 11 right), but when I queried the whereabouts of the Heath model in order to photograph it for posterity, I was informed that it no longer existed because Mary-Joe (another Rice graduate student) had eaten it. So all tangible record of a truly remarkable edifice was lost for all time.

Since the geodesic dome concepts had played such an important part in helping us to arrive at the solution (at least as far as I was concerned), I suggested that we name the compound buckminsterfullerene. Smalley and Curl fortunately agreed, accepting that though the name was long, it did indeed roll smoothly off the tongue. Thus we avoided the fearful international conflict over terminology which would have raged had we named it after a certain well-known ball game. Smalley could not resist putting some alternative suggestions for names at the end of the publication. The name engendered the occasional mild criticism[38] which was dispatched with a little help from Shakespeare.[39] Now that some time has passed, it is satisfying to note how instructive (about geodesy) others have found the name and how flexible it has turned out to be. The whole family of closed cages can be appropriately named—fullerenes.[40] The paper[41] was dispatched by Federal Express to the journal *Nature* on the afternoon of Wednesday, September 11th, 1985.

Five Long Years in the Desert

The ten-hour nonstop flight home to England was a physical and psychological high for me. My first action upon entering the house was to open the cardboard box and take out the stardome which had influenced my deliberations during the search for the structure of C_{60}. It had always looked beautiful; now it positively glowed. When the news of our result spread, Martyn Poliakoff at Nottingham wrote that his friend, David Jones, had already thought of hollow carbon cages. In 1966 Jones had written a delightful article under the pseudonym Daedalus in the journal *New Scientist*[42,43] in which he had suggested that the high-temperature process in the production of graphite might be modified to generate graphite balloons. This was a typical example of the presciently "crazy" ideas of Jones. I thus learned about the Euler principle, which says that 12 pentagons are needed to close a network and that hexagons alone just will not do. I was introduced to D'Arcy Thompson's elegant book[44] and learned that one could close an even-numbered carbon cage with any number of hexagons (except one, I subsequently learned) provided 12 pentagons were included in the network. The beautiful Aulonia (Fig. 13 photograph from Tibor Tarnai) already knew more than we about these simple (pentagonal) facets of (its) life. This was all fun and truly

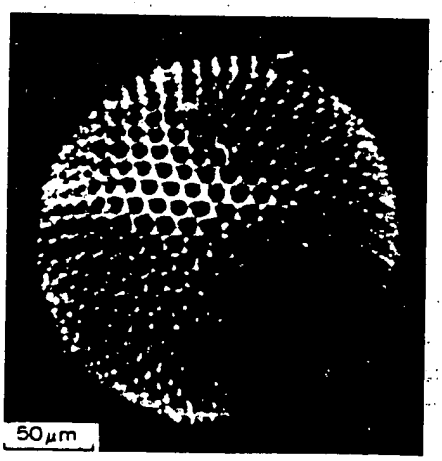


Fig. 13. A siliceous sea creature, *Aulonia hexagona*, appears at first glance to possess a skeleton composed completely of hexagons. Pentagonal structural elements are discernable, however (photograph supplied by Tibor Tarnai).

fascinating, because it became clear that there might even be other (even-numbered) carbon cages—there were certainly other (even-numbered) peaks (Fig. 6), in particular C_{70}. O'Brien and Smalley reached the same conclusions independently. Particularly important were a series of reactivity ex-

periments carried out by O'Brien, who showed that all the even-numbered carbon species were totally unreactive, a result neatly commensurate with closed structures for all the even-numbered cages.[45]

I met David Jones, a most fascinating individual, who epitomizes so much of what the spirit of science should be about. We also learned that Osawa and Yoshida had already thought of C_{60} in 1970 and had even suggested that it might be superaromatic.[46, 47] In 1973 Bochvar and Gal'pern[48] also published a theoretical paper on the molecule. Thus it transpired that although there were some most imaginative scientists around, few—other than Orville Chapman at the University of California at Los Angeles (UCLA)[49]—had noticed these pioneering flights of imagination.

Circumstantial Evidence for the Identity of the "Third Man"

The first question stimulated by the realization that we might have found a "third form of carbon" with a hollow, cage structure was obvious: is it possible to trap an atom inside the cage? My early Sheffield background led me to wonder whether iron might form an intriguing ferrocene-like analogue. The day I left, Heath tried to encapsulate iron without success, but the next day he succeeded in detecting a stable $C_{60}La$ complex.[50] This experiment provided the first convincing piece of evidence to support our proposal of the cage structure. Then began what was to become a truly exhausting schedule for me: Every four to six weeks I flew to Houston, and after two to three weeks' work with the group at Rice I returned to the UK and my commitments in Sussex. As soon as I arrived in Houston I would present a group seminar based on ideas which I had developed while in the UK. This schedule continued until April 1987. From the outset the joint Rice/Sussex follow-up program had two clear objectives. First, to make enough C_{60} to prove beyond doubt that our structure was correct and second, to measure the optical spectrum of C_{60} which we had surmised might in some way be responsible for the Diffuse Interstellar Bands.[41] These astronomical features had of course been partly responsible for the carbon-cluster experiment in the first place. These goals were all-consuming and we often talked about "the little yellow (Smalley's guess) or pink (my guess) vial" of C_{60}.

During the late 70s and early 80s I felt that it was simply not enough just to detect the carbon chains; the source must be tracked down. This obsession with the source led ultimately to the discovery of C_{60}. After 1985 I developed a similar attitude to C_{60}. Our discovery of a species which probably had a truncated icosahedral structure was "not enough", and as months and then years passed, confirmation of the structure and its identification in space also became somewhat of an obsession. We (the Rice group and myself) were convinced from the outset that our proposed structure was correct; surely it was too beautiful and perfect to be wrong. However, if for once aesthetics were misleading us, it would be much better if we proved our model wrong ourselves. It is certainly fair to say that the proposed structure was greeted with scepticism by some, though many loved C_{60} and were convinced that we were right from the start. During this period (1985–1990) I examined the problem independently at Sussex, as well as in collaboration with the Rice group, who also made independent studies. In time all these efforts resulted in a mass of convincing evidence in support of our proposal.

From the moment we discovered that C_{60} was stable I had one all-consuming dream: I wanted so solve the molecule's structure by NMR spectroscopy. Because all 60 carbon atoms in buckminsterfullerene are equivalent, the ^{13}C NMR spectrum should consist of a single line. Proof of our radical proposal in such an exquisitely simple manner was to remain elusive for some five years; this goal was almost like a holy grail—far, far beyond reach. I was quite convinced that a clever young organic chemist would accomplish this task. I had one consoling thought, namely that we had been rather successful in the past with a series of molecules whose identifications were based on spectra consisting of single lines: Phosphaethene, $CH_2=PH$ (the first phosphaalkene made) had been assigned by its $J = 1 - 0$ microwave line[1, 4] and HC_5N and also HC_7N had both been originally single radioline detections in space.[20, 22] Then there was, of course, the 720 amu peak in the mass spectrum of C_{60}.[41] How fitting it would be to round it all off by *proving* by another *single* line that C_{60} was buckminsterfullerene.

C_{70} and the Fullerene Family

It is fair to say that I (and perhaps also my colleagues at Rice University) occasionally woke up in the middle of the night and wondered whether I should have to commit suicide if our idea turned out to be wrong. Had we stuck our necks out too far? These thoughts only lasted seconds. I would reassess all the evidence, realize that everything fitted, and go back to sleep convinced more than ever that C_{60} had to be a geodesic cage. Time pased, we made several advances,[51, 52] and each time the cage concept clarified our observations. That was important. I remembered hearing Richard Feynman on BBC radio say that it seemed to him that if a radical new theory were right, it would allow the solution of previously unsolved puzzles. I quantified this: If an idea fitted 80–90% of the observations, it was almost certainly right; if more than 10–20% of the details had to be bent to fit, it was almost certainly wrong. Buckminsterfullerene was well up in the first category.

I remember vividly the day on which all my lingering doubts vanished. I was sitting at my desk thinking about the reasons why C_{60} might be stable. The missing piece of evidence in this personal jigsaw puzzle turned out to be so simple, it was almost child's play; indeed it evolved from my playing with molecular models of various conceivable cages. The solution was related to the C_{70} signal which always popped up prominently when C_{60} was strong. I used to call the two species "the Lone Ranger and Tonto"[*] because

[*] The Lone Ranger und Tonto were a famous cowboy and Indian duo from the movies. As a child I saw them every week fighting crime in the Wild West. Bob Dylan immortalized them in the following blues text:
Well the Lone Ranger and Tonto
They are ridin' down the line
Fixin' ev'rybody's troubles
Ev'rybody's 'cept mine.
Somebody must a tol' 'em that I was doin' fine.

they were so inseparable and because C_{60} was always dominant (Figs. 6 and 8). As far as C_{60} was concerned, it seemed no accident that the modern soccerball with the same layout is one of the most, if not *the* most, resilient of constructs, able to survive being kicked around the world (and perhaps around the galaxy). Maybe the football held a simple clue. When I looked carefully at a football, I was struck by the fact that all the (black) pentagons are isolated, whereas all the (white) hexagons are linked. It is known that unsaturated compounds composed of abutting pentagons (the pentalene configuration, Type **II**; Fig. 14), without substituents which allow extended conjugation, tend to be unstable. Curiously, a compound with just such a structure appeared on the cover of *Angewandte Chemie* (July 1987) that very week.

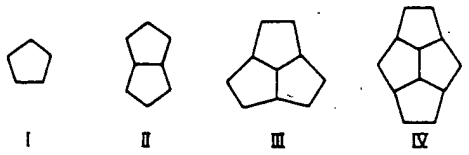


Fig. 14. Isolated and abutting pentagons: **I**, isolated; **II**, fused pair (pentalene configuration); **III**, symmetrically fused triplet (triquinacene configuration); **IV**, directly fused quartet [53].

Since Euler's law requires 12 pentagons for closure, it was also clear that C_{60} was the smallest carbon cage for which all the pentagons could be isolated. O'Brien's reactivity experiments had convinced us that closure was possible, even probable, for all the even clusters. I conjectured that a *pentagon isolation rule* could be formulated to account for the stability[53]; then I began to wonder which was the next cage for which pentagon isolation was feasible.

By playing with the models I saw immediately that it was not C_{62}, and as I added more atoms, try as I would, I could not find cage structures for C_{64}, C_{66}, or C_{68} without abutting pentagons. We had already proposed a structure for C_{70},[50] after Smalley had shown that by splitting C_{60} into two C_{30} hemispheres a ring of ten extra carbons could be neatly inserted, producing a most elegant, symmetric, egg-shaped structure (Fig. 15 right). Suddenly I realized that perhaps this C_{70} cage was the next structure after C_{60} which could close and which also had *isolated* pentagons (Fig. 15). This surprised me. Perhaps closure *necessitated* that 70 be

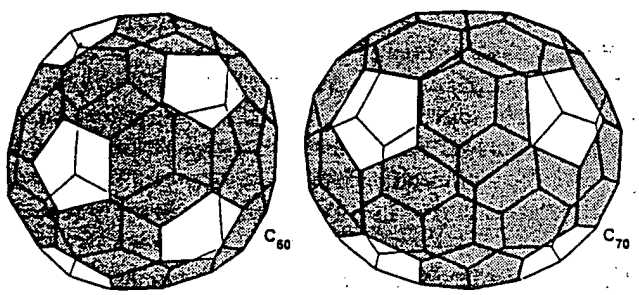


Fig. 15. For species with less than 72 atoms these two structures are the only ones which can be constructed without abutting pentagons. Thus on the basis of the *pentagon isolation principle* and geodesic considerations C_{60} and C_{70} are predicted to be the first and second magic fullerenes. This result together with Figure 8 provided the simplest and strongest circumstantial evidence supporting the closed-cage concept.

the second magic number! We had stuck our necks out with the C_{60} hypothesis on the basis of a single peak in the mass spectrum, but it now seemed that the cage concept positively insisted that C_{70} *as well as* C_{60} are special.[53] That would be wonderful. A second solution which required both of these particular magic numbers was impossible to conceive, especially since 70 would be an unusual number to be deduced as magic at all, let alone the second in order. I knew that nature would not be that perverse, and thus for first time my conviction that our structure was corrrect became absolute, and I never again doubted that one day we would be vindicated. Indeed in my opinion this result meant that we were home and dry.

I was elated by this line of reasoning, but I really needed proof. I remembered that Tom Schmalz and his colleagues, Klein and Hite, in nearby Galveston had published some elegant graph-theoretical studies on the fullerenes. I contacted him and asked him what he thought about my idea. I was amazed and delighted when he told me that they had been looking at this same problem and had proven that cages composed of 62, 64, 66, and 68 atoms cannot be constructed without abutting pentgagons.[54] So it was true! I told him that I wondered whether the semimagic C_{50} might be the smallest cage able to avoid abutting triplets of pentagons (Type **III**, Fig. 14, Lit.[53]). Schmalz et al. subsequently showed this also to be correct.[54] One Sunday afternoon, sitting in front of the molecular models strewn all over our coffee table at home, I decided to investigate other semimagic numbers. I wondered about C_{32} which had been shown by the group at Rice University to be the first cage relatively stable towards photolysis. I toyed with the idea that it might be the smallest cage able to avoid fused quartets of pentagons (Type **IV**, Fig. 14). I tried to make the smallest model containing such a structure, and as I counted up the atoms I suddenly realized, that it was not C_{32} but a delightfully symmetric C_{28} cage (Fig. 16). I became excited because I

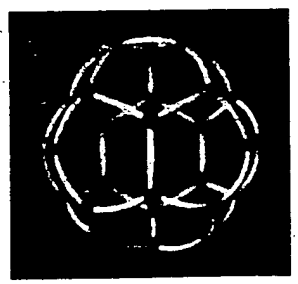


Fig. 16. Molecular model of C_{28}, one of several fullerenes (with 24, 28, 32, 50, and 70 atoms) predicted to be stable on the basis of geodesic and chemical considerations [53]. These magic-number predictions fitted almost perfectly the observations made under certain clustering conditions [51, 55] (see Fig. 17).

knew, that during the Rice/Sussex collaboration period we had occasionally obtained mass spectra in which C_{28} was almost as dominant as C_{60}. At this point it seemed that essentially all the magic numbers would fall into place if these clusters were *all* cages. In particular, I found that I could explain the fascinating spectrum (Fig. 17) published by the Exxon group.[55] Here was all the proof I needed to convince myself that a whole family of cage molecules was sitting around waiting to be discovered. The first somewhat

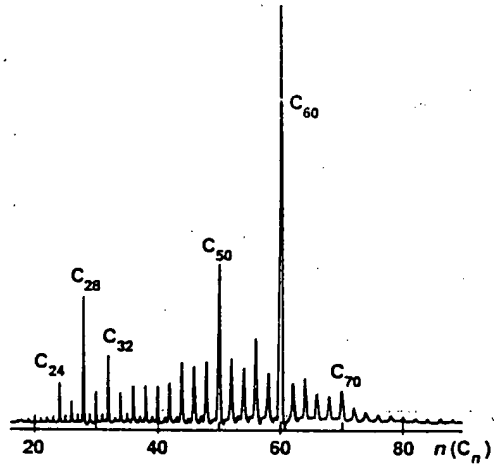


Fig. 17. The particularly interesting mass spectrum of C_n clusters obtained by Cox et al. [55]. The correspondence with the magic fullerene sequence 24, 28, 32, 50, 60, and 70 [53] was the most convincing evidence for the existence of the fullerene *family* prior to the extraction breakthrough. The sharp cut-off at 24 is particularly convincing, since no C_{22} fullerene can exist.

stable member of the family appeared to be C_{24}. This can be explained by the fact that C_{22} cannot exist (I am indebted to Patrick Fowler for pointing out this fact to me) and that C_{20} is the smallest cage and as it has no hexagons at all, almost certainly the least stable. To some extent C_{28} (Fig. 16) became my own personal favorite, because regardless of which of the four threefold axes one views this tetrahedral molecule along, it looks uncannily like Gomberg's famous free radical, triphenylmethyl; this also just had to be right. I knew about Moses Gomberg's discovery from my favorite organic text (Fieser and Fieser[56] which Harry Heaney, my chemistry teacher in school, had encouraged me to buy and read so long ago). It had always amused me to think that on attempting to make the rather mundane compound hexaphenylethane, Gomberg failed (miserably), produced the triphenylmethyl radical, and had to be consoled with becoming known as the father of free radical chemistry instead. This was the sort of "failure" that really appealed to me. If C_{28} is relatively stable, then $C_{28}H_4$ should be a fairly stable hydrofullerene. This seemed not at all farfetched; after all, dodecahedrane which Paquette and co-workers first made[57] is basically the perhydrofullerene of dodecahedrene (fullerene-20), the simplest and probably the least stable of all the fullerenes since it contains no hexagons. At this time I had a telephone conversation about nomenclature with Alex Nickon in which we came to the conclusion that the name "fullerenes" would work well for the family of carbon cages.[40, 53] I gained much satisfaction from the refined concept which was even more appropriate, because Buckminster Fuller had patented constructs of all shapes and sized based on the 5/6 ring principle;[58] some were very similar to the elongated framework of C_{70}. Nickon was just finishing his entertaining book with Silversmith on the origins of the trivial names of compounds.[40]

In Houston a particularly important series of experiments was carried out by Curl, Smalley, and their co-workers which offered further overwhelming evidence for closed cages.[52] One of these was a photofragmentation experiment which provided even-numbered products. Curl had worked out a neat way of explaining how the cages might "spit out" even-numbered (2, 4, 6, ...) carbon chains and then reseal. Another most convincing study showed that when the encapsulation of atoms of various sizes appeared to be successful, the smallest caged species detectable had diameters commensurate with the known sizes of the encapsulated atoms.

C_{60} and Soot

During one of my eight visits to Rice University between August 1985 and April 1987 we considered carefully the reactivity results and developed a hypothetical mechanism for the formation of C_{60}.[45] Heath, O'Brien, and I spent hours in the library digging through an excellent selection of books and journals on carbon. The final version of the mechanism grew out of intense synergistic group discussion. It was also clear that the mechanism might explain soot formation as well. After all in a review on soot, Harris and Weiner[59] had pointed out the complete absence of knowledge of the chemistry involved in soot formation. Thus a fresh idea probably would be welcome. Our mechanism implied C_{60} should be a by-product of soot formation. Curl was apprehensive about introducing the word soot, especially in the title. How prescient were his worries! However, Smalley and I decided to throw caution to the wind—after all, when you have gone as far as you can go (in postulating C_{60} formation in a chaotic plasma), you might as well go further. Our paper met with some criticism.[60] To our delight, however, in 1987 we heard that Klaus Homann's group in Darmstadt discovered that C_{60} was a dominant ion in a sooting flame.[61] (Note: Very recently, a careful study by Howard's group at the Massachusetts Institute of Technology has shown that up to 7% of the soot from a benzene flame consists of fullerenes.[62])

The Giant Fullerenes

One day I decided to spend £300 on ten-thousand sp^2 carbon atoms (molecular models!) The odd eyebrow was raised at Sussex when I said that I was buying them just because I wanted to see what giant fullerenes such as C_{6000} (with a diameter ten times that of C_{60}) looked like. Ken McKay (a graduate student) obtained Coxeter's book[63] and Goldberg's paper[64] and set to work. When he came into my room with models of C_{240} and C_{540} (Fig. 18), I was delighted but perplexed—they were beautiful, but not at all what I had expected. C_{540}, in particular, was not round like Buckminster Fuller's domes, but in fact much more interesting: It was essentially a monosurface which swept between cusps in the vicinity of the pentagons; it had icosahedral symmetry, but was not an icosahedron.[65] Then we realized that its shape might explain[65] the polyhedral patterns in graphite microparticle electron microscope pictures published by Iijima (Fig. 19).[66] The structure of these microparticles could be nicely explained as concentric shells of graphitic carbon in which the shells had giant fullerene shapes. Few of our discoveries have delighted me more than these objects, partly because they are so elegant, but also because the exercise, which was started *purely* for fun and with no serious aim, had yielded such an apparently important result. It was also an object lesson, since I had assumed

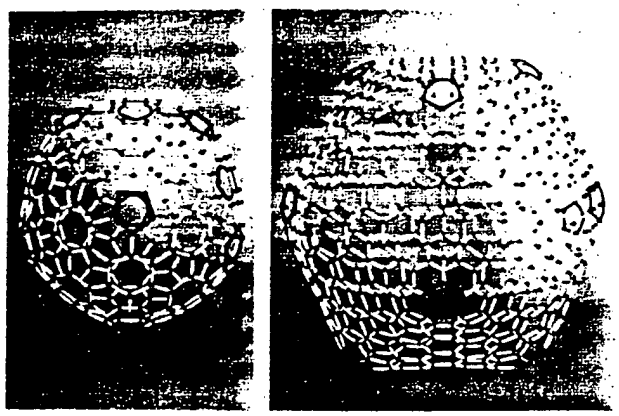


Fig. 18. Molecular models of the giant fullerenes C_{240} (left) and C_{560} (right). The models possess icosahedral shapes rather than perfectly spheroidal ones similar to the geodesic domes. Each of these structures can be considered as an initially flat hexagonal network which has warped into a closed monosurface (of icosahedral symmetry) by 12 pentagonal disclinations giving rise to the cusps.

that the giant fullerenes would be spherical like Buckminster Fuller's domes and had not looked carefully at Iijima's images. Even the most spheroidal giant fullerene (Fig. 19a) was clearly polyhedral (Fig. 19b). To see what one wants to see

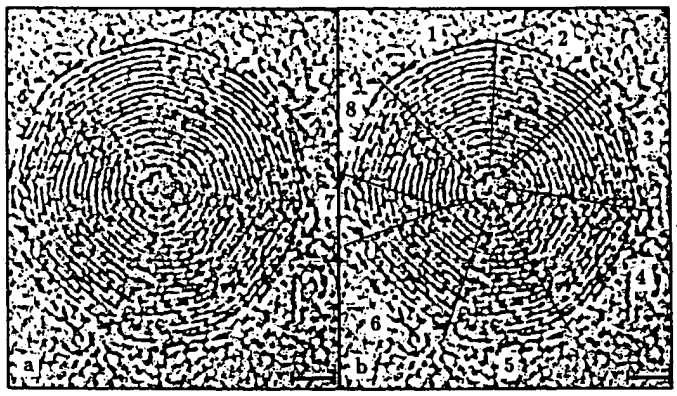


Fig. 19. The image obtained by electron microscopy of an onionlike graphite microparticle observed by Iijima [66] which appears superficially to be spheroidal (a). Careful scrutiny of this image, however, indicates that the object has a polygonal outline consistent with a set of concentric quasi-icosahedral fullerene-like shells (b) [65]. The marker indicates a scale of 20 Å.

rather than what is, is a cardinal sin for a scientist and the temptation is to be resisted at all costs.

The Quest for C_{60}

Until late 1989 the evidence in support of our structure proposal was, to my mind, very convincing, but it could not be deemed anything other than circumstantial. Clearly a macroscopic sample of C_{60} was needed—not just a whisper in a supersonic helium wind, detectable only by that ultrasensitive sensor, the mass spectrometer. At Sussex we sought more tangible evidence. The Science and Engineering Research Council (SERC) funded the construction of a cluster-beam apparatus, which was assembled with Tony Stace; Steve Wood helped us to obtain financial support from British Gas in the form of Collaborative Award in Science and Engineering (CASE) studentship for combustion-related studies. It was this assistance which was ultimately our salvation (vide infra). In a third project conducted with Ken McKay, we probed (by electron microscopy) the films produced by a carbon arc under helium in an old bell jar evaporator. We found that the film microstructure changed as the helium pressure was increased (to ca. 50 mmHg). The quadrupole mass spectrometer, with which I sought to monitor whether C_{60} was produced in this experiment, was the integral part of a modest carbon materials research project which failed to attract support from any funding source (including chemical companies). Because Stace and I had been quite generously funded by the SERC solely for the cluster-beam studies, another application (and indeed a rather applied one) to that source was difficult. Time slipped by and this program faltered even though I had put a great deal of effort into trying to obtain financial support.

The First Paper by Krätschmer, Fostiropoulos, and Huffman

In September 1989 Michael Jura (UCLA Astronomy Department) sent me a copy of a thought-provoking paper[67] (Fig. 20) presented by Krätschmer, Fostiropoulos, and Huffman at a symposium on interstellar dust. This research group from Heidelberg and Tucson had observed four weak but distinct infrared absorptions in a film of arc-processed graphite, which were tantalizingly consistent with the expected spectrum of buckminsterfullerene. From theoretical studies[68] it was known that C_{60} should exhibit only four lines. What was more, the observed frequencies agreed quite well with those predicted. I had long followed the work of this group and knew that they had developed great expertise in studying carbon by spectroscopy. We had occasionally tried related studies, and I was only too aware of how tricky they were. I was sceptical about their result and also rather cha-

Harry - Presented at Capri -
do you believe this? -H.

SEARCH FOR THE UV AND IR SPECTRA OF C_{60} IN LABORATORY-PRODUCED CARBON DUST

W.Krätschmer, K. Fostiropoulos *Max-Planck-Institut für Kernphysik, Heidelberg, W.-Germa*
and
D.R. Huffman *University of Arizona, Tucson, Arizona, USA*

Carbon dust samples were prepared by evaporating graphite in an atmosphere of an inert quenching gas (Ar or He). Changes of the spectral features of the carbon dust were observed when the pressure of the quenching gas was increased. At low pressures (order 10 torr), the spectra show the familiar broad continua. A high pressures (order 100 torr), narrow lines in the IR and two broad features in the UV emerge. The four strongest IR features are located in the vicinity of the lines predicted for the C_{60} molecule. One of the observed UV features may be related to the known 368 nm transition of C_{60}. It thus appears that at high quenching gas pressures C_{60} is produced along with the carbon dust.

Fig. 20. Annotated copy of the key paper presented by Krätschmer, Fostiropoulos, and Huffman at the conference *Dusty Objects in the Universe* in Capri (1989) [67]. This paper with the appended query was sent to me by Michael Jura (UCLA) who attended this conference.

grined. for had not Ken Mc. .y and I made soot in a bell jar in exactly the same way three years before during the project, which we were forced to abandon through lack of funds?

I decided to resurrect the old and decrepit bell jar and with Jonathan Hare (holder of the British Gas CASE graduate studentship) tried to reproduce the infrared features obtained by Krätschmer et al. Michael Jura's missive arrived around September 1989, just before the start of the Sussex academic year, a time when third year undergraduate projects are needed. It does not matter whether these projects yield results; they should imbue the student with the flavor and excitement of genuine research, that is, the experience of working in the dark, not—as all too often happens—the frantic scramble for results at all costs! I had often initiated the most speculative of projects in this way, and my experience had shown time and time again that important and exciting studies could often start from such inauspicious beginnings. It seemed perfect for Amit Sarkar's third-year project, and he joined Hare on this wildly speculative project. Fairly soon these students succeeded in obtaining the IR bands (Fig. 21), which, although always very weak and highly irreproducible, confirmed the observations of the group from Heidelberg and Tucson. The obsolete apparatus then

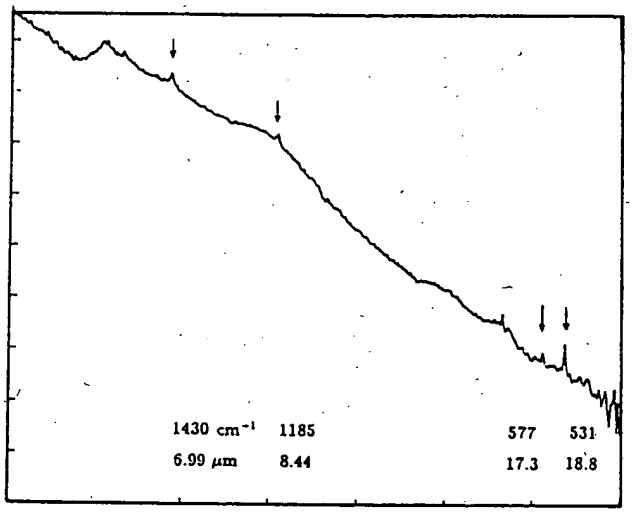


Fig. 21. Infrared spectrum of a film of arc-processed carbon obtained by Hare and Sarkar at Sussex which shows weak but clear (and confirmatory) evidence that the features first observed by Krätschmer et al. [67] (see Fig. 20) and tentatively assigned to C_{60} were real and repeatable.

promptly fell to pieces! After rebuilding it almost completely from scratch, Hare tried to repeat the earlier observations, but consistent results eluded him. Sometimes he obtained the characteristic spectral features, sometimes they disappeared for days or weeks at a time. In retrospect, I suspect that the original discovery of the IR features by Krätschmer et al. could have been made by few other groups. Hare carefully varied every experimental parameter he could think of and finally developed the expertise to produce films which exhibited the telltale infrared features consistently. He wrote to Krätschmer about his efforts and received an encouraging reply containing useful advice. This certainly helped, because it was quite difficult to make films amenable to analysis.

The Dimerization of C_{30}

I spent about one month in the UCLA Astronomy Department around Easter 1990. One day, Mark Morris brought François Diederich from the Chemistry Department to see me. Diederich appeared excited and exhorted me to come to his office because he had something to show me. In response to his manner I somewhat disdainfully quipped, "You've not made C_{60}?" When he replied, "How do you know?", I was startled and suddenly became apprehensive since there was genuine surprise in his voice. When we arrived at his office he showed me an astonishing mass spectrum. In their attempts to make a pure carbon ring of 30 atoms Diederich, Rubin, Whetton, and their co-workers, had found that the molecule spontaneously dimerized to form C_{60} with almost unbelievable efficiency.[69] This staggering result seemed to answer, almost at a stroke, many puzzling questions that had been on my mind for years about carbon chains, their relationship with C_{60}, and soot. But I became even more apprehensive when I comprehended that the UCLA group might be on the verge of obtaining the coveted C_{60} NMR line. Subsequent discussions with David Walton, with whom I had probed aspects of the C_{60} formation mechanism,[70] alleviated my worries; he convinced me that scaling up the UCLA experiment so as to produce sufficient C_{60} for the key NMR measurement presented an anormous challenge.

Mass Spectrometry

I returned to Sussex and by early summer 1990 started to believe for the first time that C_{60} really might be in our sooty deposit. We therefore decided to probe the material by solid-state magic-angle-spinning (MAS) NMR. Indeed Ken Seddon (a Sussex colleague) had encouraged me to do this some years before. Perhaps the single ^{13}C NMR line was close at hand in the black soot, which at least we could now touch. I considered buying the most isotopically pure ^{13}C graphite, but that would have been very expensive, and we had no

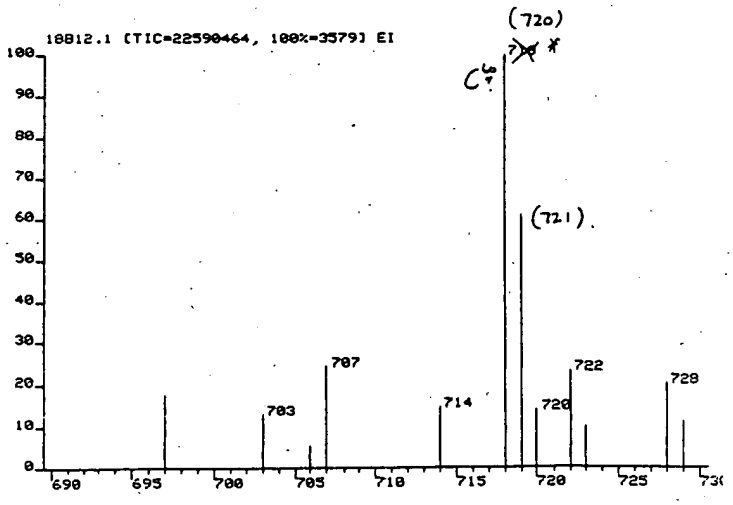


Fig. 22. Part of the FAB mass spectrum of a deposit of arc-processed soot obtained by Abdul-Sada on July 23rd, 1990 at Sussex. The calibration was off by 2 amu; however, the isotope pattern was convincing since the peaks are close to the intensity ratio 1.0/0.66/0.44 expected for $^{12}C_{60}/^{12}C_{59}/^{12}C_{58}\,^{13}C_2$.

money anyway. The problem of generating enough material for solid-state NMR from the scrapings of thin sooty films, seemed insurmountable, especially since it was so difficult to produce the films in the first place, let alone analyze them. We really needed another way to monitor the samples, so we tried Fast Atom Bombardment (FAB) mass spectrometry. Ala'a Abdul-Sada helped us, and finally we obtained the mass spectrum shown in Figure 22. The signal containing the ^{13}C satellites was really quite convincing, but I wanted the result confirmed. The entry in Jonathan Hare's laboratory notebook on July 26th, 1990 (Fig. 23 top, second sentence) epitomizes many of our problems and requires little further comment.

The Red Solution

During this period we had considered the properties of C_{60}. What form would the compound take? Would it be a high-melting solid or a liquid? Would it be soluble? Benzene was an obvious solvent, since C_{60} should look like benzene from every side (or at least from 20 sides). I remembered the little pink (or yellow) vial of liquid we used to talk about and wondered if the compound might even be volatile. In addition I had often discussed (with Smalley, Rohlfing, and others) how much C_{60} was being made in our experiments. The rough proportion which always seemed to arise was $<1/10000$ of the total amount of carbon. At this level, given the amount of soot available, only a supreme optimist would attempt solvent extraction. Fortunately Hare is one—perhaps partly because he is a physicist working among chemists. On Friday, August 3rd Hare made up a mixture of the soot and benzene in a small vial, which he set aside over the weekend (Fig. 23, second entry). When he came in on Monday morning (August 6th) he noted (Fig. 23, third entry) that the solution looked "slightly red(d)ish" (Fig. 24). The generation of a red solution from pure carbon was scarcely believable. Hare made more material during the next few days and attempted mass spectrometric measurements on extracted material for the first time on Thursday, August 9th (Fig. 23, fourth entry).

possible use of FAB Mass Spect. 26/7/90.

Came back from Scotland Walk to find Fab Mass Spec had been done with exciting results. unfortunately the machine has been clean so we can't repeat.

Results so far.

Seen decent signal @ (12xC) = 720amu !

also ^{13}C is ~1% of natural carbon so calculations show that for C_{60} we 60% could have One

3/8/90

1) Made spot ½ a (30ml) tube of C_{60}^{δ} + Carbon powder, Actual Volume would be much smaller than this bcos powder is so uncompact.

2) added about 25ml of Benzene and shook mixture

3) allowed to stand for Weekend.

6/8/90

Solution looks slightly reddish, tried to pipet liquid out from top but mixed up.

9/8/90

Vacume lined sample to about 5th of Volume could go lower (ie more concentrated) but we need about this Volume if we want to use IR liquid cell, so will keep to this.

(Continued evaporation down to about 4-5 drops (but ?). FAB showed No C_{60} (720).

Fig. 23. Entries by Hare in his laboratory notebook: July 26th, 1990; August 3rd, 1990; August 6th, 1990; August 9th, 1990.

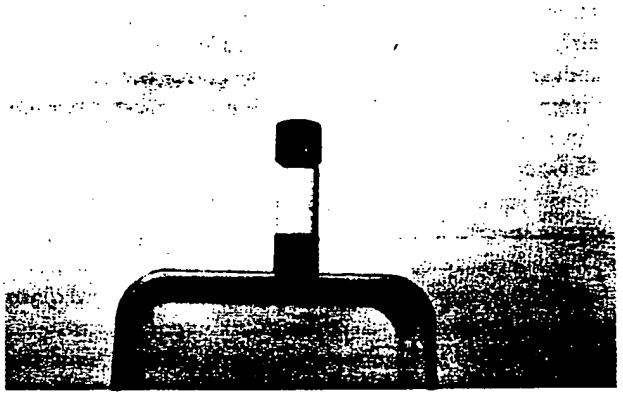


Fig. 24. Original reddish extract obtained on Monday, September 6th, 1990 (see Fig. 23).

About 10 o'clock the next morning (Friday, August 10th) I received a telephone request from the journal *Nature* to referee a paper by the Heidelberg/Tucson group which I accepted. I was totally unprepared for the bombshell which arrived minutes later by telefax. Following up their own earlier work, Krätschmer, Lamb, Fostiropoulos, and Huffman had successfully sublimed from their carbon deposit a volatile brown material, which dissolved in benzene to give a RED SOLUTION (!!!!!).[71] Crystals obtained from this solution yielded X-ray and electron-diffraction data commensurate with material composed of arrays of spheroidal molecules 7 Å in diameter separated by 3 Å, just as expected for buckminsterfullerene. This beautiful paper even contained photographs of crystals. I was convinced that they had isolated C_{60}, and we had been pipped at the post. Somewhat stunned, I pondered our demise and faxed my report back to *Nature* after lunch. I recommended that the paper be published without delay and requested the editor to convey my sincere congratulations to Krätschmer and his associates.

This was what the British call a difficult moment, but as I slowly surveyed the damage I realized that all was not quite lost. It gradually dawned on me that there was not a single(!) NMR line to be seen in the manuscript (nor was there a mass spectrum. We later learned that they had the mass spectrum, but certain problems had arisen which precluded its inclu-

sion in the manuscript.) At this point we had spent nearly a year struggling independently learning how to make the arc-processed material: we had made our own soot, we had confirmed the presence of C_{60} mass spectrometrically, and we had solvent-extracted the red materal—and all this *before* the manuscript arrived. I decided that we were not going to abandon our efforts now after we had achieved all this. We still had a lot going for us, and I thought we might be able to obtain the desired NMR result. However, now that the Heidelberg/Tucson study was essentially in the public domain it would be transmitted around the world by telefax within hours. I had studiously tried to avoid such situations in science—competition—all my life; my philosophy is to probe areas in which few others, preferably no one, work. That is where, it seems to me, the most unexpected discoveries are likely to be made.

We had to act very quickly if five years of effort were not to be completely in vain. A race must be on because the material was now so easy to make, and it could not be long before other groups, far better equipped than we, recognized that there was one last exquisite prize remaining in the story of the discovery of C_{60}—the NMR line. Our one priceless advantage was that Hare had already made a reasonable quantity of material, and that, at that moment, only the Heidelberg/Tucson group had any at all. We needed help and fast. Roger Taylor, an organic chemist, provided the desperately needed expertise; he separated the material quickly and efficiently. Since our mass spectrometer had broken down again, Hare rushed by train to Manchester with a sample of the precious extract. Numerous frantic telephone calls passed between Sussex and Manchester, because the sample refused to respond to analysis. Then with a key piece of

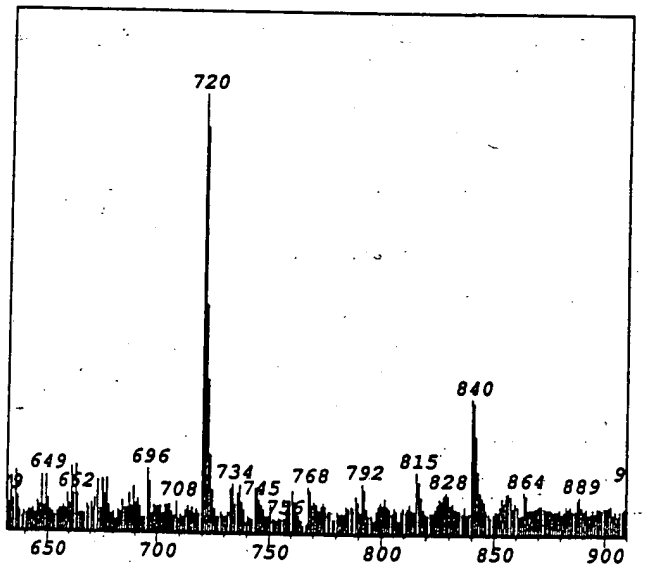


Fig. 25. Part of the FAB mass spectrum of the red extract which confirmed that it consisted mainly of C_{60} and C_{70}. The spectrum also indicates the presence of other fullerenes [72].

advice from Taylor about solubility, the Manchester operators (at Kratos) managed to dissolve the material in the FAB matrix and obtained the FABulous mass spectrum shown in Figure 25. It was hard to believe, but besides C_{60} other fullerenes with 56 to 72 atoms were detected; in particular, C_{70} was abundant. The whole family of fullerenes appeared to be present in the soot, not just C_{60}!

C_{60} is Magenta (Pink?) in Solution

Taylor noted that the extract was soluble in hexane and recognized that he might be able to separate the fullerenes chromatographically. To his delight he found that on an alumina column resolution into two bands, one red, the other magenta, could be achieved. The magenta fraction, (Fig. 26) was a delight to the eye in the delicacy of its color.

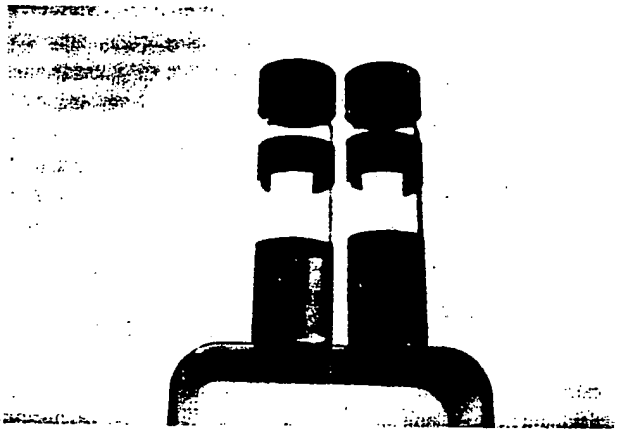


Fig. 26. Chromatographic separation of the red extract by Taylor resulted in a magenta C_{60} fraction (left) and a red C_{70} fraction (right).

Its mass spectrum showed a peak at 720 amu, and we sent the sample to Tony Avent for NMR analysis. We were summoned to see our single line (Fig. 27), which Avent assured

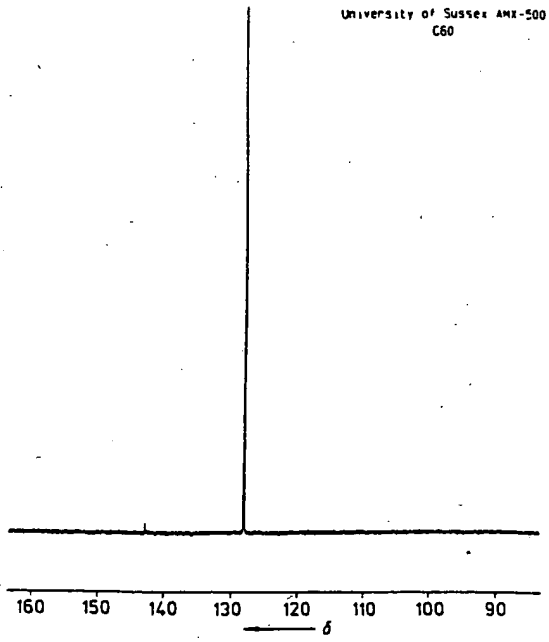


Fig. 27. The first NMR spectrum in which the C_{60} resonance (at $\delta = 143$ ppm) was first identified (barely). The strong line at $\delta = 128$ ppm is (rather appropriately) the resonance of benzene.

us was present. So this was it: a line so small I needed a microscope to see it! Could this insignificant little blip really be the line I had dreamed about for five years? Further work confirmed beautifully that this was the result which we had sought for so long.[72] The joy alleviated almost all the despair I had first felt on reading the paper by Krätschmer et al. One might have thought, as some said, that I should have been pleased to have been proven right when so many had been sceptical. That was not my feeling, probably because I had known ever since the recognition of C_{70} as the second magic fullerene[51] that our structure could not possibly be wrong. I know that my colleagues at Rice University also had no doubts.

What about C_{70}? It turned out to be the icing on the cake, although not without attendent trauma. The wine-red fraction which had masked the pale magenta of C_{60} yielded a mass spectral peak at 840 amu and was clearly C_{70}. According to the expected structure (Fig. 15 right) this compound should exhibit a ^{13}C NMR spectrum with five lines. On Sunday, September 2nd, 1990 I entered the laboratory at the same time as Avent who told me the C_{70} measurement should have just been completed. The spectrum we plotted was sensational—or almost so. There were indeed five lines, but one was in the same position as the C_{60} peak. Could it be that one line was underneath the C_{60} signal? After repeated chromatography to remove the last vestiges of C_{60}, further NMR studies showed the fifth line to be rather different from the others. The resonance of the ten atoms in the waist (Fig. 28c) is more "benzenoid" than the other four resonances.[72] Indeed this line lies dangerously close to the benzene solvent line: had it been a little closer to the benzene signal it would have been swamped and missed altogether. In many ways the five lines of C_{70} are (arguably) more important and significant than the C_{60} singlet. For one thing, they confirm that fullerene carbon atoms are not fluxional; for another, they show that the atoms are not on the perimeter of a monocyclic ring. Both of these cases would lead to a spectrum with a single resonance. Even more important was the fact that the NMR results confirmed the family concept for fullerene cages. It was now clear that a host of stable fullerenes were just waiting to be discovered, as we had long suspected.[53]

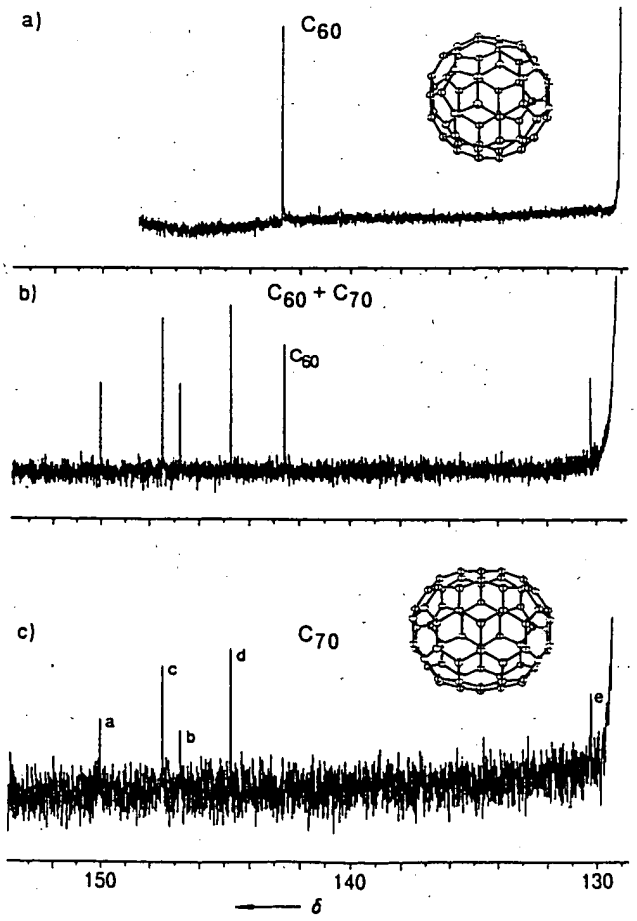


Fig. 28. ^{13}C NMR spectra obtained from chromatographed samples of soluble material extracted from arc-processed graphite: a) spectrum of purified C_{60} (magenta fraction); b) mixed C_{60}/C_{70} sample; c) spectrum of purified C_{70} (red fraction) showing five lines as expected for the symmetric egg-shaped molecule (see Fig. 15).

"The Third Man" is as Elusive as Ever in Space

The elusiveness of C_{60} and my belief that it has been lurking in that blackest of black materials, soot, since time immemorial often reminded me of the role played by Orson Welles in the film "The Third Man". The spirit of this antihero pervades the whole movie although he is seldom seen. Indeed he makes his first appearance late on in the movie in the black shadows of a dark street in Vienna when his face is suddenly illuminated by a light being switched on. For five years C_{60} played a very similar shadowy role—at least as far as I was concerned. My part in the buckminsterfullerene story really started out in space, and this celestial sphere has come down to earth with more of a bounce than a bump; but will it bound back up into space? Is this third form of carbon distributed ubiquitously in space as we surmised the day we found it in the laboratory?[41] Now that we know something about fullerene-60, we should be able to study all its optical properties. It is clear that the UV radiation density in the optically observable interstellar medium is such that the species will be ionized.[73] The possible existence of encapsulated complex ions[73, 74] is quite interesting. However, even with buckminsterfullerene in our hands, we find that this "third man" is as elusive as he ever was in the space between the stars. Perhaps the interstellar form is related to protonated carbon monoxide (HCO^+), which Bill Klemperer identified about 20 years ago.[17] If there are any C_{60} molecules in space there can be little doubt that most will have a proton or some other atom adhering to their surface.[74] $C_{60}H^+$ could probably survive for eons. Other abundant elements, particularly alkali and alkaline-earth metals, must also stick to the surface. Such species will have fascinating optical spectra. For instance, the energy and wavelength of the charge-transfer transition $(C_{60}^+)X \rightarrow (C_{60})X^+$ can be estimated to a first approximation as simply the difference between the ionization potentials of the separated species. For $(C_{60}H)^+$ this transition lies at about 2200 Å. For $(C_{60}Na)^+$ and $(C_{60}K)^+$ the transitions lie in the region of the Diffuse Interstellar Bands[33] and for $(C_{60}Mg)^+$ near zero frequency(!) These observations imply that this and related species will have unusual electrical properties. These processes are probably related to the recently observed superconductivity

of metal-doped fullerene-60 materials.[75] This conjecture is supported by an important new result which comes not from work with bulk material but from cluster-beam studies by McElvaney and Callahan.[76] They found that the gas-phase proton affinity of C_{60} is similar to that of ammonia—a remarkable result! I like to put my trust in intuition: when all else fails it is, after all, our only guide: It is curious to note that some important spectral features of space (the Diffuse Bands) have been visible for decades, yet we do not know what causes them. Now we have discovered that an unexpected molecule, C_{60}, has been under our noses on earth since time immemorial and was invisible until now. It seems to me highly likely that these two observations will turn out to be connected.

Epilogue

Since the time that graphite balloons and C_{60} were twinkles in the eyes of David Jones, Eiji Osawa, and a few other imaginative scientists,[42, 43, 46–48] there have been many significant contributions, both experimental and theoretical, to the first chapter of the buckminsterfullerene story which has just been completed. These have recently been comprehensively reviewed.[77] Figure 12 shows the Rice/Sussex team and Figure 29, the Sussex Buckaneers. These two teams together with the Heidelberg/Tucson team scored many of the goals in the football match which has just ended. Many new teams have now started to play an exciting, but different, ball game. The important difference is that the players can now see what they are kicking.

Fig. 29. The Sussex Buckaneers football team. From left: Kroto, Abdul-Sada, Taylor, Hare, and Walton.

Apart from the successful observation of the "lone" NMR line, two other matters give me a sense of deep pleasure: one was the beautiful color of C_{60} and, furthermore, that it was seen first at Sussex. The second was that apparently no one else appeared to have followed up the early IR results obtained by the group from Heidelberg and Tucson (September 1989). In retrospect I find this astounding; perhaps it was because the work appeared in the astronomy literature, but more likely it was because research today is carried out under such pressure, and our fear of failure is so great (and exacerbated by funding procedures). Few groups enjoy the luxury of working in the dark—a condition which I feel lies at the heart of true scientific endeavor. I have a videotape of a marvellous BBC documentary on Richard Feynman (the greatest lecturer I had ever heard) from the series "Horizon". In one part he talks on essentially this topic. This 50 minute program had the most profound effect on me. At one point Feynmann described how, when he was hired at Cornell, Bob Wilson had told him that it was the university's responsibility whether he accomplished anything—it was their risk(!) It was not for Feynman to worry about, he should amuse himself. In this way he was freed from the psychological burden of doing anything "important", and he was able to relax and do what he most enjoyed—physics and mathematics—just for the fun of it. How lucky he was. I know of few professional scientists today, certainly no young ones, who are in such a utopian scientific environment. What a sad reflection on today's research, especially since we know in our hearts that human beings achieve most when they are free of pressure. We know that small children learn and discover the joys of nature most efficiently during their play.

News of the breakthroughs spread like wildfire during September 1990, and the method of production developed by the Heidelberg/Tucson group was immediately improved upon[78] at Rice University. As soon as it was known that fullerenes are chromatographically separable and that solution NMR is feasible, other groups confirmed these measurements.[79, 80] Don Huffman remarked laconically at a recent symposium, "Everyone is able to repeat these experiments".

A new postbuckminsterfullerene world of round organic chemistry and materials science has been discovered overnight. Almost every day a new paper appears on some novel aspect of fullerene behavior. The group from Rice University has shown that C_{60} forms species such as $C_{60}H_{36}$.[78] Hawkins et al. have made an osmium complex in which the spinning of the fullerene ball is stopped and has enabled accurate bond lengths to be determined.[81] NMR studies by Yannoni et al. have also yielded accurate bond lengths.[82] The radical anion has been polymethylated by Olah's group;[83] platinum complexes have been prepared at DuPont.[84] At AT&T it has been found that the metal-doped material now holds the temperature record for molecular superconductivity.[75] Fascinating differences in the crystal structure of C_{60} have been found which depend upon how the crystals are produced.[77] Foote and co-workers at UCLA have shown that C_{60} transfers light energy efficiently to generate singlet oxygen.[85] Diederich, Whetten, and co-workers have evidence for oxides such as $C_{70}O$.[86] C_{60} is decomposed by light under circumstances which still need to be fully identified.[87] Also interesting is the fact that more fullerenes, such as C_{76} and C_{84}, are being extracted and characterized.[86] The fullerene family has arrived in force, and there are balls of all shapes and sizes for everyone to play with.

This advance is an achievement of fundamental science, not applied science, and serves as a timely reminder that fundamental science can achieve results of importance for strategic and applied areas. The origin of the whole program lay in an interest in aspects of molecular dynamics, allied

with the quest for an understanding of the origin of the carbon chains in space and their possible relationship to circumstellar and interstellar grains as well as soot.[1] These ideas welded together beautifully with the major advance in cluster science brought about by the experimental techniques developed by Smalley and co-workers at Rice University. Krätschmer and Huffman and co-workers were originally motivated by an interest in space dust and, in their recent breakthrough, by astrophysical implications of C_{60}. The C_{60} story has many facets, but more than anything else it is yet another archetypal lesson on the benefits to be gained by supporting pure fundamental science. The field has exploded, and its applications in chemistry and the science of materials are only just starting to be explored. Finally it is worth noting that C_{60} might have been detected 20–40 years ago, perhaps in a sooting flame; one wonders why it took so long.

Another lesson may be learned from these acknowledgements. Important contributions were made in research programs at the University of Sussex (Brighton, UK), the National Research Council (Ottawa, Canada), Rice University (Houston, Texas, USA), the Max-Planck-Institut für Kernphysik (Heidelberg, Germany) and the University of Arizona (Tucson, USA). The discovery of C_{60} is a tribute to not only the international nature of science but also the necessity of interdisciplinary cooperation. The contribution from the University of Sussex to the story started as a consequence of the "Chemistry by Thesis" degree course initiated by Colin Eaborn, which enabled undergraduates (such as Anthony Alexander) to carry out research with supervisors from more than one field. It could only have been successful in the interdisciplinary scientific research and teaching environment which the university pioneered when Sussex was founded in the "optimistic 60s". Sadly this and other courses have been "regulated" out of existence by bureaucrats who have little understanding of how student research expertise is brought to maturity and no awareness of the dire consequences for our future scientific capability. The first part the story could also not have been achieved had chemistry at Sussex been divided into those traditional subsections of organic, inorganic, and physical chemistry. I also had close contacts with astronomers at Sussex, particularly Bill McCrea and Robert Smith. The carbon discoveries resulted from a free-wheeling research program which started with synthetic chemistry (with David Walton, Anthony Alexander, and Colin Kirby) and moved via spectroscopy and quantum mechanics to radioastronomy (with Takeshi Oka, Lorne Avery, Norm Broten, and John MacLeod at the NRC). It moved back to the laboratory and chemical physics (with Jim Heath, Sean O'Brien, Bob Curl, and Rick Smalley at Rice University). In the last phase, key advice came from Michael Jura (an astronomer) which initiated some basic chemistry (with Jonathan Hare, Amit Sarkar, Ala'a Abdul Sada, Roger Taylor, and David Walton). Apart from those mentioned in the text who played direct (and sometimes crucial parts) such as Steve Wood of British Gas, I also acknowledge greatly the help of many others who played indirect parts, particularly graduate students and post-doctoral fellows as well as colleagues such as Tony Stace, Roger Suffolk, and Mike Lappert. Finally I wish to thank Ed Wasserman for some invaluable advice and David Walton in particular for his unfailing help throughout the period of this story and his painstaking assistance in preparing this account.

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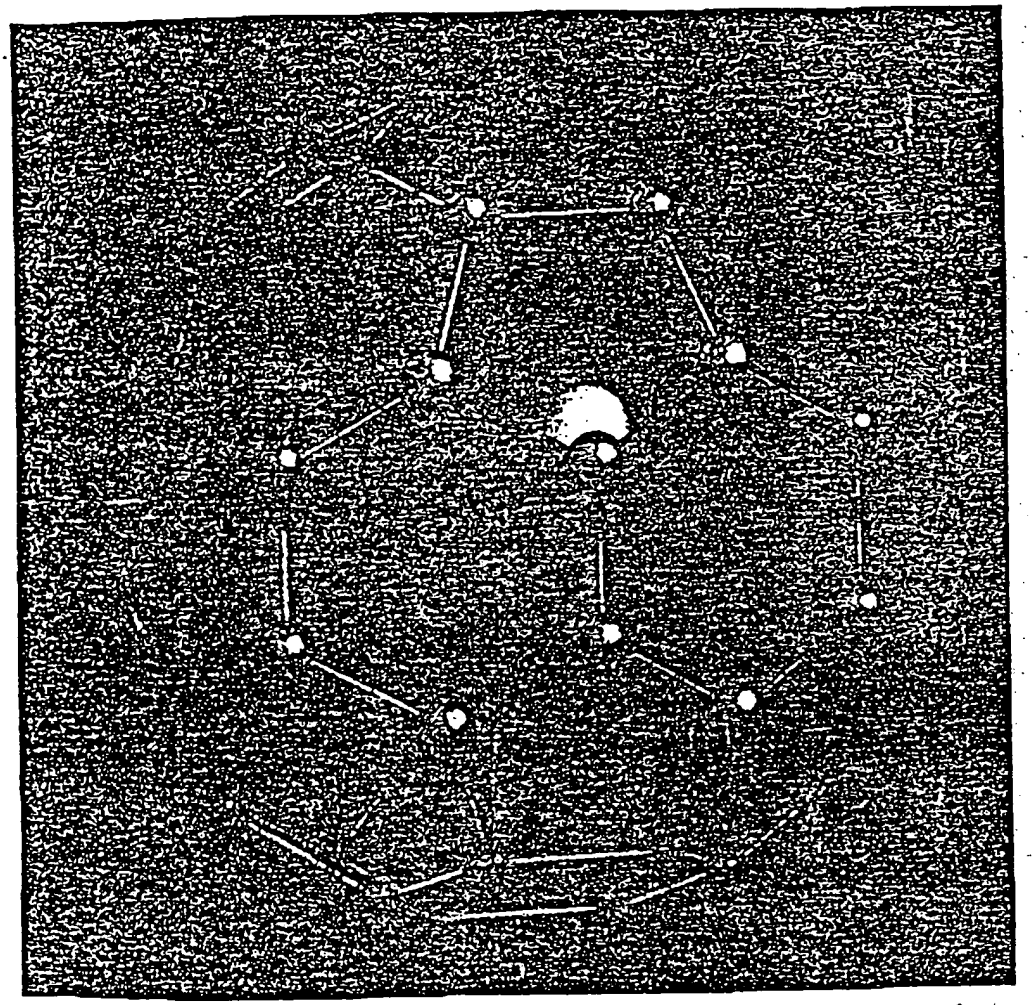
SCIENTIFIC AMERICAN

Remnants of a planet that failed to form.

Still no technological fix for oil spills.

What made higher life-forms possible?



Buckyball, the third form of pure carbon, cages an atom in its lattice.

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Fullerenes

These cagelike molecules constitute the third form of pure carbon (the other two are diamond and graphite). C_{60}, the archetype, is the roundest molecule that can possibly exist

by Robert F. Curl and Richard E. Smalley

In May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent turned red.

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their collaborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tucson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fax, exchanging measurements of the material—its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this hollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had failed. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Texas, we celebrated with champagne all around. For although we had to some extent been scooped, we had been vindicated as well. Five years earlier we had had our own Eureka! experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that C_{60} could be made in a uniquely stable form simply by laser-vaporizing graphite in a pulsed jet of helium. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Fuller, we named it buckminsterfullerene, or buckyball for short.

In addition to C_{60}, another molecule, C_{70}, appeared to be quite special in these early experiments. We soon found that the stability of C_{70} could be understood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and hexagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C_{60} has 20 hexagons, whereas the structure we proposed for C_{70} has 25, producing a shape reminiscent of a rugby ball.

In fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Fuller, it seemed fitting to term this entirely new class of molecules the "fullerenes."

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym "Daedalus" in the *New Scientist* in 1966, had conceived of a "hollow molecule" made of curled-up graphitic sheets. Others had predicted the stability of C_{60} from calculations and tried—unsuccessfully—to synthesize it. We, however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be perfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of them—billions and billions more.

Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collaborated for the past seven years in research on carbon and semiconductor clusters in supersonic beams. Curl is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quantum Institute.

HYPERFULLERENE STRUCTURE called a Russian egg is expected to form along with ordinary fullerenes in a laser-vaporized carbon plume. Shown here is the most symmetric form: a C_{60} at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in icosahedral alignment.

proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

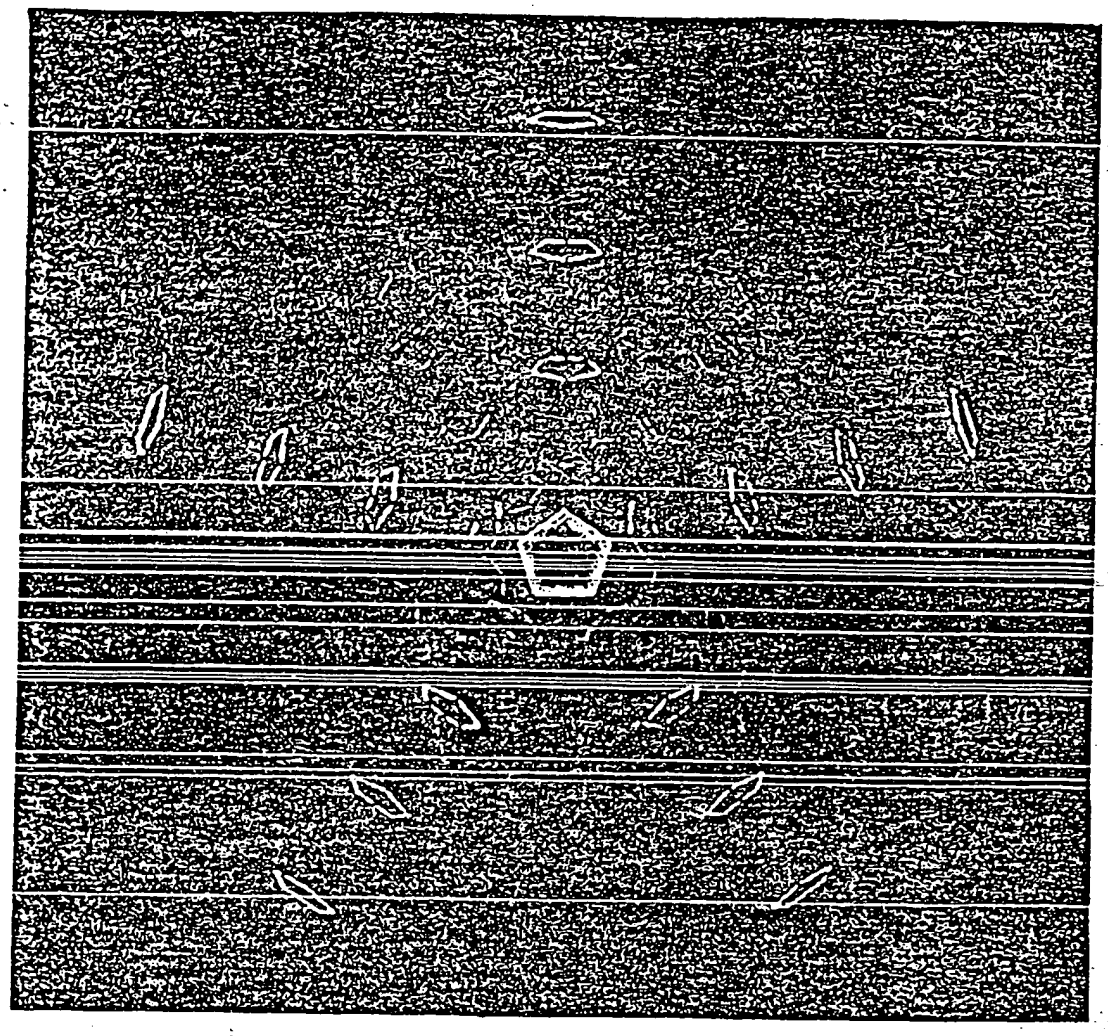
In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of C_{60}. We shirred the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

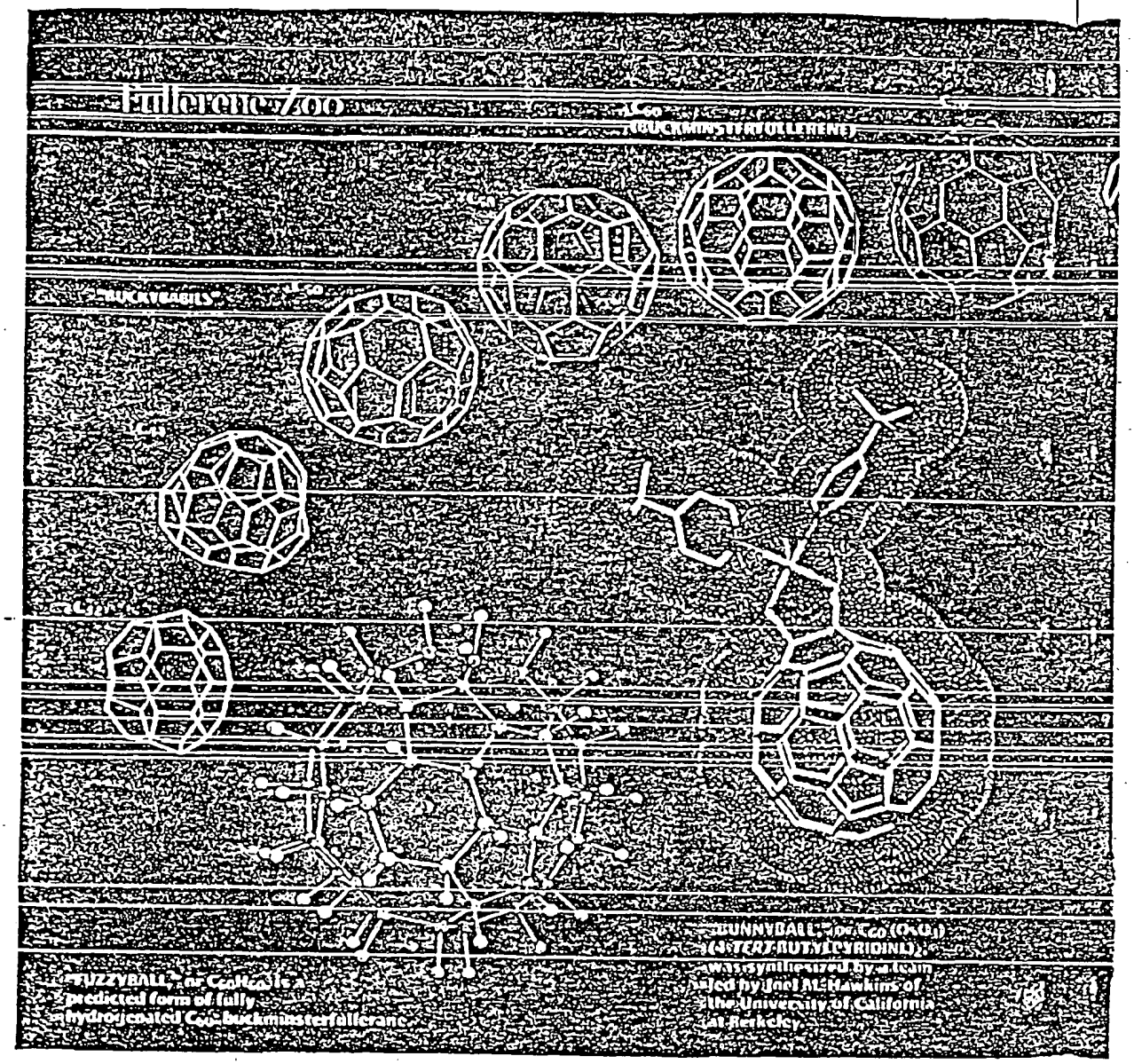
Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Perhaps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected C_{60} to be available in bulk anytime soon.

In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from observations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [*see bottom illustration on page 58*]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of

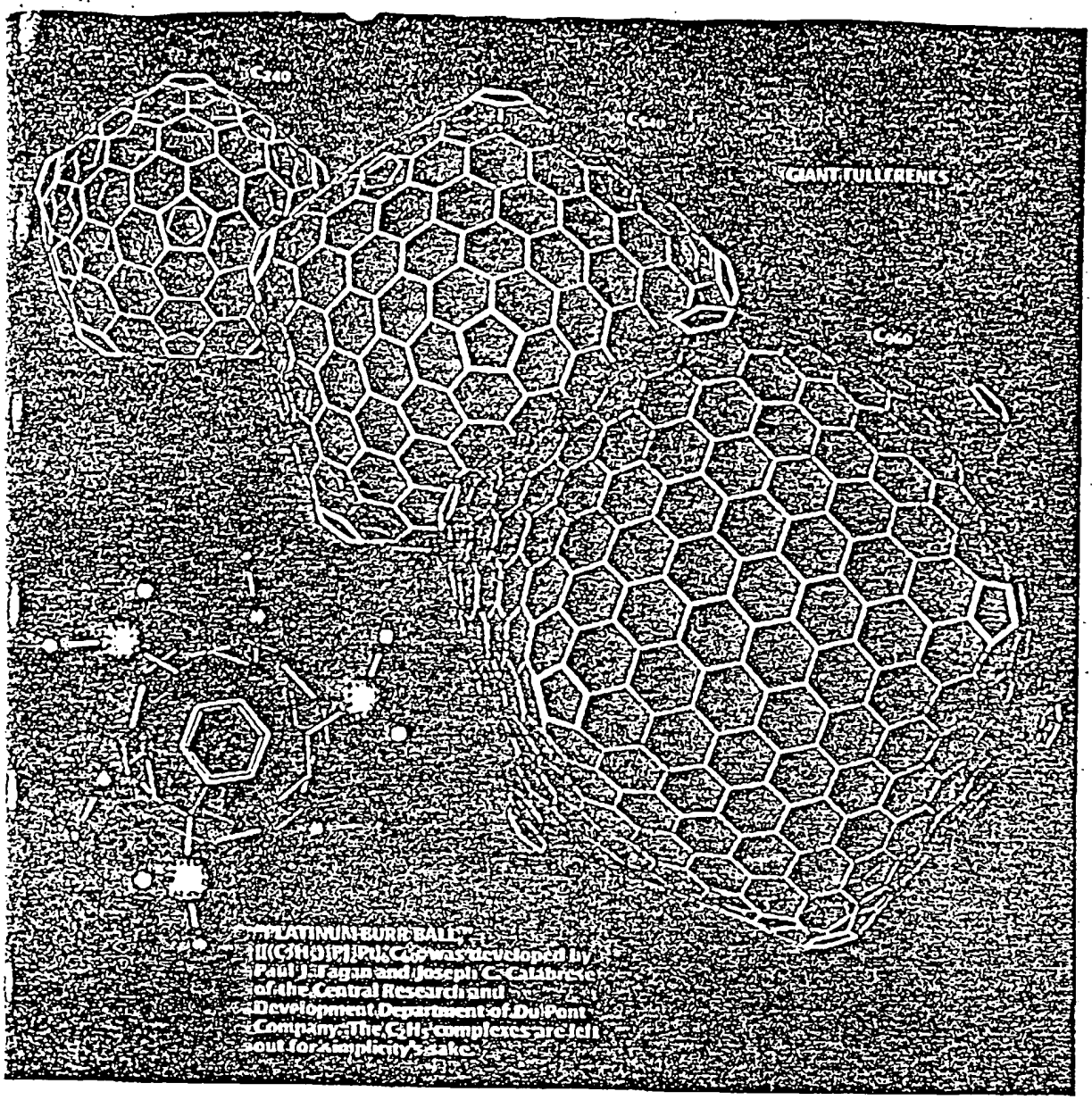




our discovery of C_{60} and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that C_{60} account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikeliness of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the C_{60} hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball C_{60}. These predictions held that of the 174 vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that C_{60} might be present in abundance.

Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-

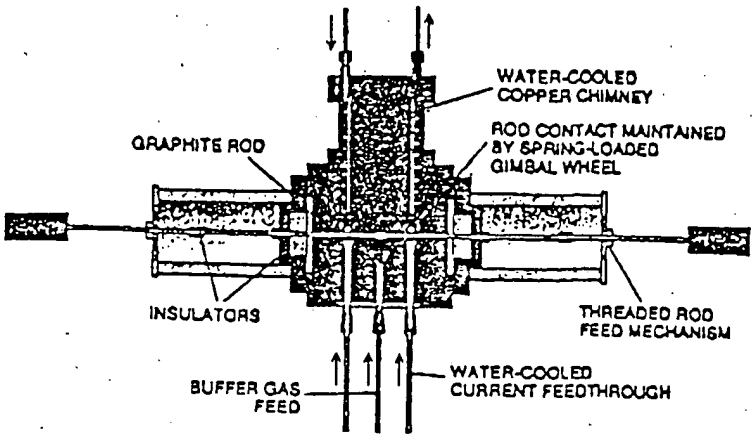


volved route. They prepared a sample from pure ^{13}C, a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of C_{60}. Because benzene molecules take the shape of a ring of carbon atoms, C_{60} would thus be seen as a kind of spherical benzene.

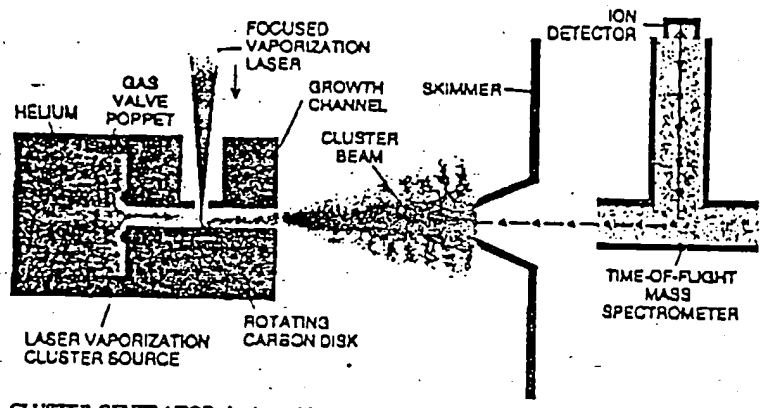
When the Kratschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials, which Kratschmer and Huffman christened "fullerite."

In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent C_{60} (the soccerball), 23 percent C_{70} (the rugby ball) and a grab bag of larger fullerenes.

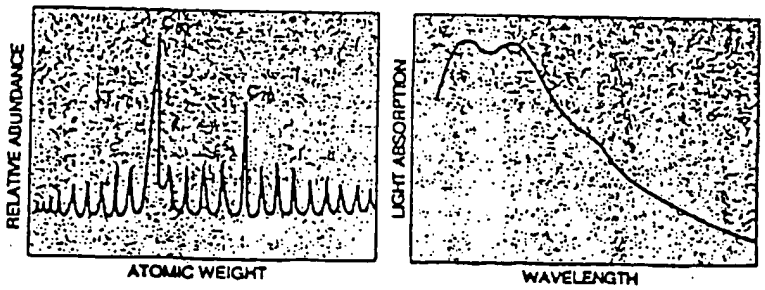
Here was a new form of pure, solid



FULLERENE FACTORY makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



CLUSTER GENERATOR designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



CRUCIAL GRAPHS: In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially C_{60}, suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain C_{60}.

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with hunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of C_{60} and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written [*see box on page 62*]. The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for C_{60} arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because C_{60} is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show.

more than 100 million times a second. The NMR experiments also dramatically verify that C_{70} has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when C_{60} molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect—C_{60} crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [*see illustration on page 62*]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of C_{60}. Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of C_{60}. In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [*see box on page 62*]—the manufacturing cost of C_{60} will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fail in the search for the yellow vial? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?

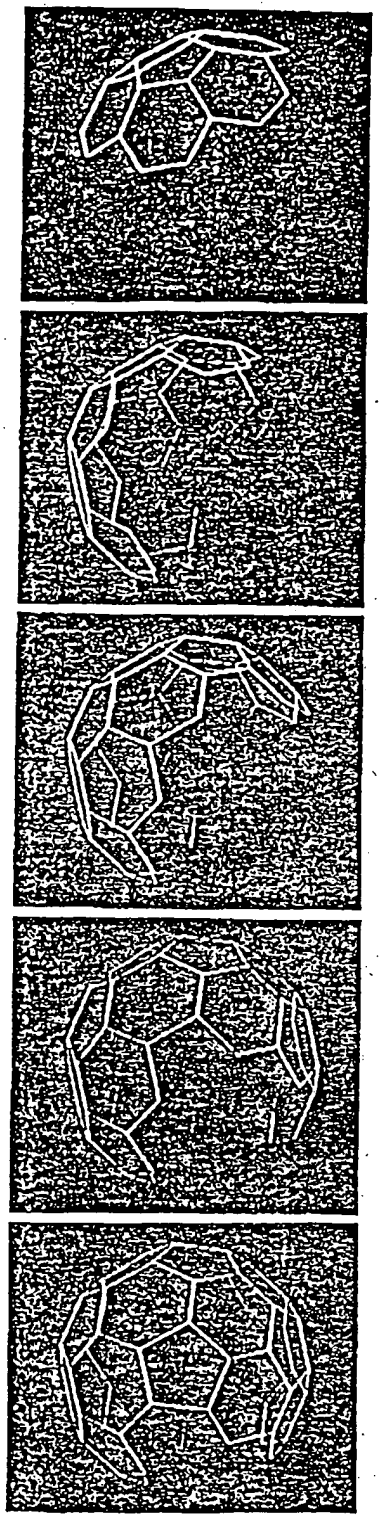
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cagelike structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of C_{60}. Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; SCIENTIFIC AMERICAN, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

Growth of a Buckyball



cally inert carrier gas, which cooled the vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members, C_{60} and C_{70}, were somewhat more abundant than their neighbors [*see bottom illustration on page 58*]. The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

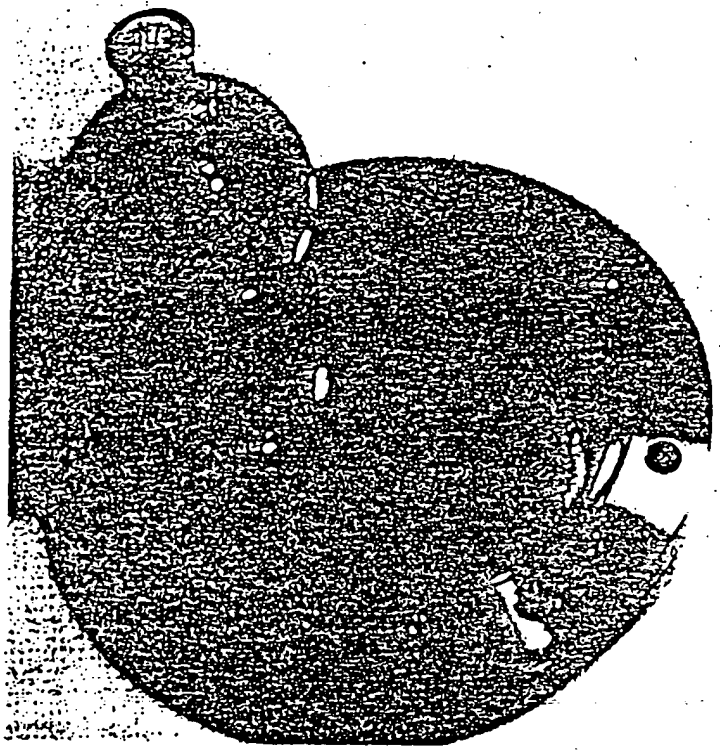
The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which C_{60} stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is C_{60}; the next is C_{70}. Although C_{71} and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained positions. This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF C_{60} depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.

FULLERENE CRYSTALS were produced by evaporating a benzene solution of C_{60} containing a significant admixture of C_{70}.

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire, these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams. Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes.

Chemists are conditioned to think of

Fullerene Electronics

Currently the most technologically interesting properties of bulk C_{60} are electronic: in various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when C_{60} molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk C_{60} has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope, C_{60} with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that K_3C_{60} is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

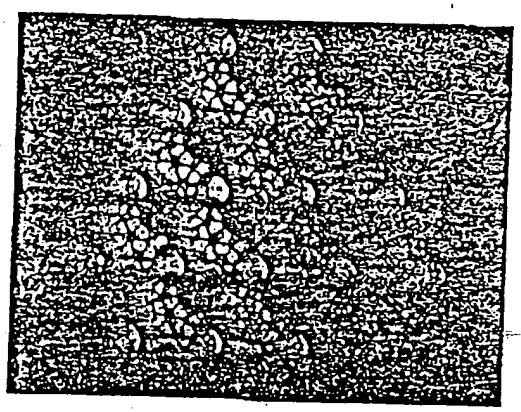
The Bell Labs team further discovered that this K_3C_{60} metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium–doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

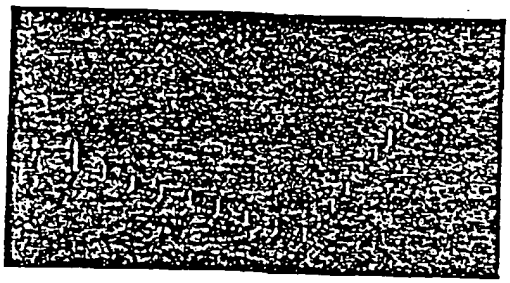
The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered C_{60} films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the K_3C_{60} superconductor can also be made [*see micrograph at right*], and the interface between the C_{60} crystalline film and the K_3C_{60} material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to learn how to dope them selectively to make *n*-type and *p*-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the C_{60} cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk C_{60} seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparelleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ($C_{60}F_{60}$). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.





SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of K_3C_{60} (*diagram*), producing a crystal that can be grown on a gallium arsenide substrate (*scanning tunneling micrograph*).

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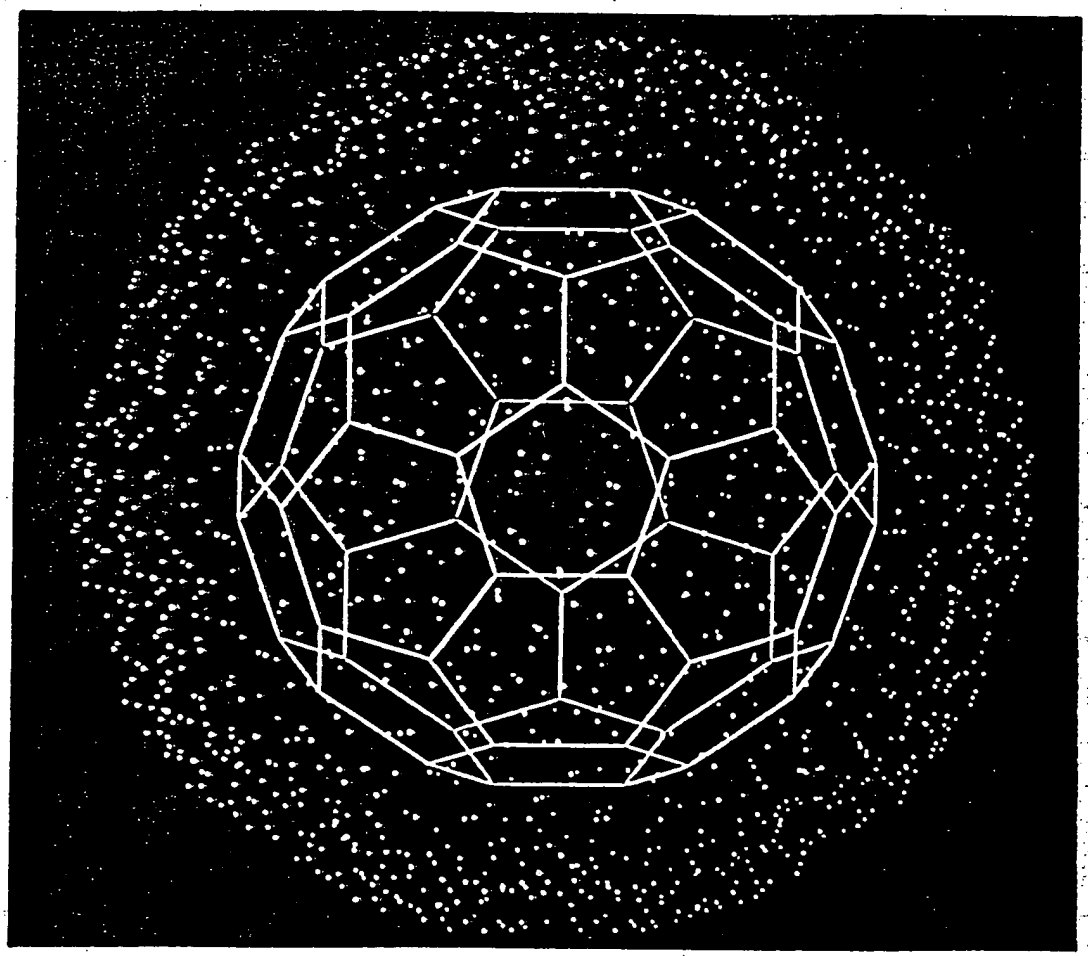

SIXTY-CARBON CLUSTER

AUTUMN BOOKS

Harvey Brooks
(transformation of MIT)

P. N. Johnson-Laird
(brain and mind)

Anthony W. Clare
(psychoanalysis as religion)

A. O. Lucas
(war on disease)

Hendrik B. G. Casimir
(physics and physicists)

Gordon Thompson
(dimensions of nuclear proliferation)

Jacques Ninio
(origins of life)

Edward Harrison
(steps through the cosmos)

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously[2-5].

The vaporization of carbon has been studied previously in a very similar apparatus[6]. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the C_{60} peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the C_{60} peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which C_{60} is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38-120 atoms resulted. The C_{60} peak was largest but not dominant. In Fig. 3*b*, the vaporization laser was fired at the time of maximum helium density; the C_{60} peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C_{70}. In Fig. 3*a*, the conditions were similar to those in Fig. 3*b* but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by C_{60}, in fact more than 50% of the total large cluster abundance is accounted for by C_{60}; the C_{70} peak has diminished in relative intensity compared with C_{60}, but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar graphite fused six-membered ring structure. We believe that the distribution in Fig. 3*c* is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp^2 valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C_{60} molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms[8].

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

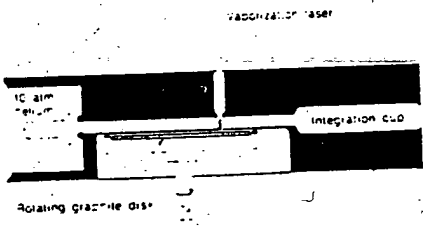

Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam (30-40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle, striking a graphite disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

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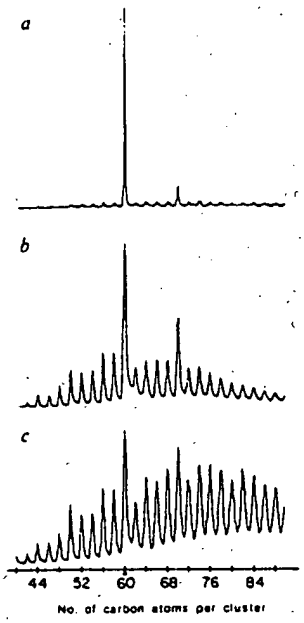

Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In *c*, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in *b* was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in *a* was obtained by maximizing these cluster thermalization and cluster–cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively, C_{60} or a derivative might be the carrier of the diffuse interstellar lines[9].

If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C_{60} derivatives of many kinds—such as C_{60} transition metal compounds, for example, $C_{60}Fe$ or halogenated species like $C_{60}F_{60}$ which might be a super-lubricant. We also have evidence that an atom (such as lanthanum[8] and oxygen[1]) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this C_{60} species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

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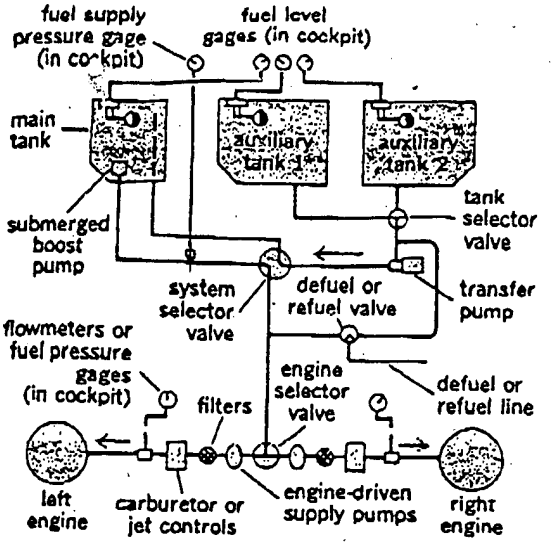


Diagram of a typical aircraft fuel system.

is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxiliary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly. [F.C.M./J.A.B.]

Fugacity A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity f_i of a constituent i of a thermodynamic system is defined by the following equation (where μ_i is the chemical

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

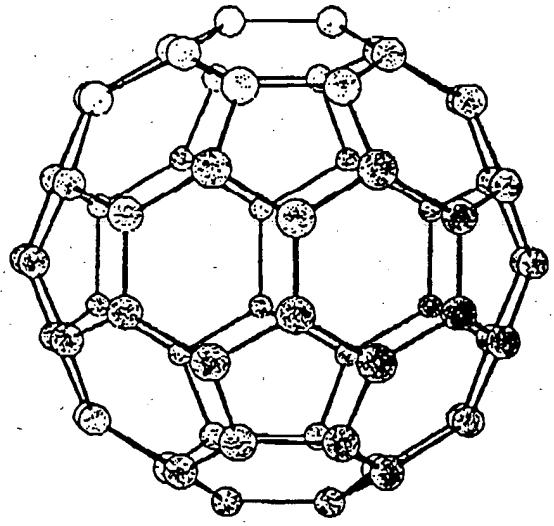
potential and μ_i° is a function of temperature only), in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value for μ_i°, which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1 atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. *See* ACTIVITY (THERMODYNAMICS); CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; GAS. [P.J.B.]

Fullerene A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. *See* CARBON.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene (C_{60} or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and n hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the sp^2 sigma-bonding skeleton, and the fourth p electron is one of 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of pi electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. *See* ELECTRON CONFIGURATION; GRAPHITE.

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammonated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom [for example, lanthanum (La), potassium (K), or calcium (Ca)] is trapped inside the cage.



Structure of C_{60} (buckminsterfullerene).

Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

Fullerene-60 was discovered as a direct result of physicochemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture. [H.W.K.]

Fuller's earth Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.

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